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Aerosol Characterization of Ambient Air Near a Commercial Lurgi Coal Gasification Plant, Kosovo Region, Yugoslavia

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Ambient air samples were collected continuously from May 14-29, 1980 to determine if the emissions from a commercial Lurgi coal gasification plant could be identified downwind of the facility. Physical, inorganic, and organic analyses were carried out on the collected aerosol samples, and organic constituents were determined on the vapor-phase sample catches.

The total atmospheric particle loading was higher immediately downwind from the Kosovo industrial complex that includes the gasification plant. Coal dust resulting from the handling, grinding and transporting of the coal was probably a major contributor to the particle burden. A very complex organic mixture was found in the vapor-phase and adsorbed on the particulate matter. Maximum individual concentrations were 8 $\mu g/m^3$ for naphthalene in the vapor and 0,08 $\mu g/m^3$ for the benzopyrene isomer group adsorbed on the particles. The naphthalene loadings were found to correlate positively with the percent of downwind sampling time. The GC-MS profile of organic compounds found in the ambient air samples also correlated well with those expected from emission sources at the gasification plant (represented by the middle oil, one of the coal gasifier's by-products). Thus the compounds found can be considered characteristic of the emissions from the Kosovo Lurgi coal gasification plant.

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ABSTRACT

An atmospheric sampling and analysis program was carried out to determine if the emissions from a Lurgi coal gasification plant could be identified in the ambient air in the vicinity of the facility. Several other sources in the immediate area also contributed to the atmospheric mixture of pollutants.

Physical and inorganic analyses were carried out on the collected particulate matter using gravimetric analysis, ion chromatography, and scanning electron microscopy. Elemental analysis was done using the inductively coupled argon plasma emission technique, proton-induced X-ray emissions and combustion analysis. Both particle catches and vapors trapped on Tenax resins were subjected to organic analysis using gas chromatography. Flame ionization detection and sulfur and nitrogen specific detectors were employed in addition to the GC-MS method in organic compound identification and quantitation.

The total atmospheric particle loading was higher immediately downwind from the Kosovo industrial complex that includes the gasification plant. Coal dust resulting from the handling, grinding and transporting of the coal was probably a major contributor to the particle burden.

A very complex organic mixture was found in the vapor phase and adsorbed on the particulate matter. Maximum individual concentrations were 8 $\mu g/m^3$ for naphthalene in the vapor and 0.08 $\mu g/m^3$ for the benzopyrene isomer group adsorbed on the particles. The naphthalene loadings were found to correlate positively with the percent of downwind sampling time. The GC-MS profile of organic compounds found in the ambient air samples also correlated well with those expected from emission sources at the gasification plant (represented by the middle oil, one of the coal gasifier's by-products). Thus the compounds found can be considered characteristic of the emissions from the Kosovo Lurgi coal gasification plant.

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SECTION 1.0

PROGRAM SUMMARY

1.1 INTRODUCTION

Radian Corporation was contracted by the U.S. Environmental Protection Agency to manage a program aimed at assessing the impact on ambient air quality of the emissions from a Lurgi-process coal gasification plant. The plant chosen for study is located in the Kosovo region of Yugoslavia. The program was an integrated effort in sampling and analysis involving personnel from Radian, the EPA, other U.S. governmental agencies and EPA contractors and grantees, in participation with the following Yugoslavian agencies: the Rudarski Institut, the Kosovo Institut, the Kombinat Kosovo and the Institut za Primenu Nuklearne Energije (INEP).

The objectives of the program were threefold:

- to sample and identify pollutants in the ground level ambient air in the vicinity of the industrial complex at Kosovo where the coal gasification facility is located,
- to determine if specific pollutants found could be identified with the Lurgi coal gasification plant, and
- to evaluate the effect of the Lurgi gasification process on the air quality in the immediate vicinity of the plant.

The program was designed to meet these objectives by providing chemical and physical data on the ambient air samples. Species believed to be emitted from the Kosovo gasification plant were of special concern.

The Lurgi process of coal gasification was selected for study because it is currently being proposed for demonstration in the United States as a commercially feasible technology for indirect coal liquefaction and synthetic natural gas (SNG) production. Assessment of the environmental effects associated with this technology is desirable before Lurgi-based plants are constructed in the U.S. A study of the gasification plant at Kosovo, Yugoslavia, represented a unique opportunity to evaluate potential environmental problems of a full-scale operating Lurgi process plant.

Radian was responsible for the overall coordination and management of the programs in sampling and analysis. Radian's scope of activities included the following tasks:

- designing and implementing a comprehensive program in quality assurance (QA) for the sampling and analysis efforts,
- providing assistance to the EPA Project Officer in the training and supervision of Yugoslavian personnel for the collection of ambient atmospheric samples,
- maintaining custody of the samples and distributing them for analysis by the cooperating laboratories in the U.S.A. and Yugoslavia, and
- the comprehensive characterization of a portion of the atmospheric samples in an analytical program which featured validation of the analytical methods used and a statistical analysis of data.

1.2 SAMPLING STRATEGY

The objective of the sampling program was to collect ambient atmospheric samples at upwind, downwind, and crosswind locations from the coal gasification plant in order to identify the effect of the plant's emission on local air quality. This involved collecting samples set at multiple sites to distinguish the contribution of the gasification plant from that due to other sources within the Kosovo industrial complex and the surrounding area. The sampling of the gasification plant's emissions was complicated by the proximity of other potential pollution sources: a coal processing unit, fertilizer plant, steam plant, and coal-burning electric generating plant, as well as steam and diesel trains and farming activity in the area.

Five sampling stations were deployed outside the perimeter of the industrial complex according to prevailing wind patterns. Atmospheric samples were collected over a sixteen day period from May 14-29, 1979. Each sampling station was equipped to collect: total particles for organic analysis; total ($<15\ \mu m$) and fine ($<2\ \mu m$) particles for gravimetric, inorganic and elemental analysis; size fractionated particles for elemental analysis; and organic vapors. The sampling equipment and the characteristic daily sampling periods were as follows:

- a high volume (HiVol) aerosol sampler with a Tenax resin organic vapor trap assembly (24 hour sample),
- a low volume (LoVol) aerosol sampler collecting total and fine fractions (6 hour samples, 4 per day),
- a cascade impactor (6 hour samples, 4 per day), and
- a time-phased particulate sampler (streaker) (7 day sample).

Two of the stations were also equipped to provide continuous records of wind speed and direction. One station also monitored temperature, solar flux, atmospheric pressure and time.

Quality assurance audits were conducted daily by Radian personnel on-site in Kosovo covering the following aspects of the sampling program: sampling media preparation, equipment calibration and operation, initial and final gravimetric measurements, sample storage and transport, and sample documentation.

1.3 ANALYSIS STRATEGY

The objective of the analysis program was to analyze the particle and vapor catches collected in the vicinity of the Kosovo industrial complex, and to compare certain identified organic species and inorganic concentrations found with similar data on the gasification plant's emissions and by-product streams. To this end, three integrated courses of analysis were followed:

- physical characterization of the particulate matter,
- inorganic analysis of the particulate matter, and
- organic analysis of species in the vapor and adsorbed on the particulate matter.

Physical Characterization

- Sub-15 and sub-2 micrometer mass loadings at each site for each time interval were determined and compared.
- Mass loadings were plotted as a function of the site's time-percentage downwind.
- Selected particulate catches were viewed and photographed using a scanning electron microscope (SEM).

The objective of these analyses was to determine the ambient aerosol burden and to distinguish the types of aerosols present (i.e., dust, coal dust, fly ash, organic material).

Inorganic Analysis

- Specific water soluble ions associated with the particles were quantified by ion chromatography (Na^+, NH_4^+, Cl^-, NO_3^-, $SO_4^=$).
- Total, elemental concentrations of 15 metals in the particulate matter were determined by inductively coupled argon plasma (ICAP) emission spectroscopy.

- Total, elemental concentrations of carbon, nitrogen, hydrogen, and sulfur in the particulate matter were determined using combustion analysis.

- The relative amounts of the principle chemical forms of carbon were determined: graphitic, carbonate, organic, etc.

- Multi-element analysis of particle catches in various size ranges (between 0.25 - 10 m) and of the particulate matter collected continuously by the streaker sampler were determined by proton-induced X-ray emission (PIXE) spectroscopy.

The analytical scheme for the inorganic species was designed to quantify the elemental and inorganic components associated with the aerosols. These data, plotted against the percentage of time that a sampling site was downwind from the gasifier, identified the pollutants that correlated with downwind collection. Some of the physical and inorganic data were useful in attempting to identify sources of the particles.

Organic Analysis

- Methods appropriate for the analysis of organic species (e.g., aromatics, organic sulfur and nitrogen species) on the Tenax resin and HiVol filter samples were developed and validated.

- Two independent means of separating the vapor phase sample from the collection matrix were used: solvent extraction and thermal desorption.

- Packed-column gas chromatography (GC) was used, followed by four complementary means of detection to achieve a detailed chemical speciation and quantitation: FID (Flame Ionization Detection), Mass Spectrometry (MS), Hall-Sulfur and Hall-Nitrogen specific detectors.

- The GC profile of the ambient organic catch was compared with the GC profile of the gasifier by-products analyzed by the same methods.

The organic analysis strategy was designed to characterize (identify and determine relative amounts of) the organic compounds in the gasifier emissions, and to carry out a program in quality assurance to validate this characterization.

Sample Distribution

Half of the samples, from days 1-4 and 13-16, were delivered to INEP in Belgrade; the rest were transported to the Radian laboratory in Austin, Texas. The subsequent distribution of samples for analysis within the U.S was as follows:

- Days 9-12 of the HiVol and Tenax resin vapor traps were sent to Oak Ridge National Laboratories (ORNL) for organic analysis.

- Days 5-8 of the HiVol and Tenax resin vapor traps were retained by Radian for organic characterization and analytical QA study.

- Days 5-12 of the LoVol aerosol samples were retained by Radian. Selected upwind/downwind pairs were analyzed for specific water soluble ions. Upwind and downwind composite samples were also analyzed for 15 metallic elements using ICAP.

- All impactor and streaker samples were sent to Florida State University for multi-element analysis by PIXE.

- Three ambient air grab sample bombs were sent to the Gas Kinetics and Photochemistry Branch, EPA/RTP.

- Selected filters were analyzed for total carbon, hydrogen, nitrogen, and sulfur for Radian by Huffman Laboratory (Wheatridge, Colorado); Radian selected upwind/downwind pairs for analysis.

- Carbon speciation was carried out by the Oregon Graduate Center.

1.4 RESULTS

Physical Characterization

- Aerosol loadings (both total and fine) were significantly greater in the samples collected downwind of the Kosovo industrial complex. The increase was greater for the coarse aerosol loading than for the fine particles.

- The particulate matter collected downwind appeared to be of mineral origin. Only small amounts (<1 percent) of typically spherical fly ash were found.

Inorganic Analyses

- Correlations between concentration (μg/m^3) and percent downwind were not found for any chemical or elemental species except total carbon. That is, the total carbon content of the aerosol mass was greater for the downwind sites. Furthermore, the percentge increase was larger for the coarse aerosol fraction than for the fine fraction.

Organic Analyses

- Several improved analytical methods developed by Radian were validated in the characterization of the air samples and gasification plant products: homogenization and quantitative aliquoting of large Tenax resin samples to achieve a greater dynamic range in its analysis; thermal desorption of sorbed vapors from the Tenax resin yielding quantitative recoveries of aromatics in a volatility range that extended from benzene (bp 80°C) to pyrene (bp 404°C); and organic speciation using sulfur and nitrogen specific detectors following the same GC column to yield profiles of the sulfur and nitrogen containing compounds against the much higher hydrocarbon background.

- The Tenax resin vapor traps were found to have collected organic species in the volatility range from benzene to pyrene. Benzene and toluene were determined to have not been collected quantitatively, i.e., breakthrough occurred for both Tenax traps. Breakthrough may have occurred for other volatile species, but the xylenes and all heavier compounds were determined to have been collected quantitatively.

- There was a clear distinction (although some overlap) between organic compounds adsorbed on the particulate matter caught on the HiVol filter and in the vapors sorbed on the Tenax resin. The aromatic vapors spanned from benzene (Molecular Weight 78) to pyrene (MW 202). The filter samples contained polynuclear aromatics (PNA's) from naphthalene (MW 128) through the benzopyrene isomeric group (MW 252).

- Mass spectrometric analysis succeeded in tentative identification of more than 50 organic compounds and isomeric groups (distributed over 12 categories defined in the Multimedia Environmental Goals) present in the atmospheric samples. The list of identified compounds included: alkylated benzenes through at least C_4 substitution, PNA's and alkylated PNA's through benzopyrenes, linear and heterocyclic hydrocarbons, phenols, ketones, quinones, alkylated pyridines and quinolines, alkylated thiophenes and dibenzofuran.

- Quantitation by MS and FID places the maximum individual species concentration in the ambient samples at $\sim 8\ \mu g/m^3$ for naphthalene in the vapor phase and $\sim 0.08\ \mu g/m^3$ for the benzopyrene isomer group adsorbed on the particulate matter when extrapolated to 100 percent downwind. Minimum detected concentrations were a factor of 100 to 1000 less than these maximum values. Comparison of measured concentrations with AMEG (Ambient Multimedia Environmental Goal) values indicates that certain species (i.e., benzopyrene isomers) may cause harmful health effects.

- The organic compounds detected in the air samples were almost identical to the compounds found in certain emissions from the coal gasification plant.

1.5 CONCLUSIONS

- The increase in particulate matter collected downwind of the Kosovo industrial complex can probably be attributed to mechanical sources, such as coal crushing, sizing and transporting.

- Measured ambient concentrations of certain organic species, such as benzopyrene isomers and organic sulfur- and nitrogen-containing compounds, emitted from the Kosovo coal gasification plant may be sufficient to cause harmful health effects based on EPA's Multimedia Environmental Goals.

- There appears to be a strong positive correlation between the organic compounds found in the ambient air samples and those expected from emission sources at the gasification plant (represented by the middle oil). This correlation suggests that is is possible to differentiate between the emissions from the gasification plant and those from other sources within the Kosovo industrial complex.

1.6 RECOMMENDATIONS

From the results and conclusions reached in this program and from the results of source testing at the gasification plant, a comprehensive ambient sampling and analysis program around the Kosovo Lurgi plant is recommended. Specific elements of this proposed program would include:

- determination of the transport and fate of the major and minor pollutants which were identified in this study as being emitted from the Lurgi gasification plant. These pollutants include vapors (benzene), sulfur gases (H_2S, COS, methyl and ethyl mercaptans, thiophenes), nitrogen-containing species (ammonia and pyridines), and PNA's (benzopyrene isomers);

- additional elemental and mineral analyses of collected particulate matter and coal dust to identify the actual contribution of the gasification plant to the ambient aerosol burden;

- development and validation of improved sampling and analysis techniques for quantitative collection of low molecular weight gases and organic vapors (i.e., benzene, mercaptans, ammonia, pyridine, etc.); and

- correlation of ambient air pollutants to point sources in the gasification plant.

Any further sampling efforts should resolve the wind corridors into twenty-two 1/2° segments for a better definition of "downwind"; this is particularly necessary at greater distances (>2km) from the source.

Other specific recommendations from this study include:

- Identification and quantitation of heavy organics (i.e., 5-, 6-ring PNA's) by alternative analytical techniques such as high pressure liquid chromatography.
- Identification and quantitation of organic compounds in the lignite to determine if the coal is a source of heavy organics.
- Assessment of the atmospheric chemistry associated with the compounds identified in the Lurgi plant's emissions (i.e., mercaptans, benzene, H_2S, COS, NH_3, etc.).

SECTION 2.0

KOSOVO ATMOSPHERIC SAMPLING PROGRAM

The objectives for the sampling of the ambient air outside the perimeter of the Kosovo industrial complex were:

- quantitative sampling of both the particulate matter and the organic vapors in a way that would permit subsequent elemental, inorganic and organic analysis;
- differentiation of emissions attributable to the coal gasification plant from other emissions in the area; and
- validation of the sampling program with a comprehensive QA program executed concurrently with sample collection.

The sampling program was a cooperative effort involving personnel from the EPA, Radian, Northrop Services, Inc., and several Yugoslavian institutions. An organization chart for the aerosol sampling program is shown in Figure 2-1.

The following sections describe the industrial complex and its emission sources, the location and operation of the sampling sites, and the methods of sample collection and handling.

2.1 KOSOVO INDUSTRIAL COMPLEX: COAL GASIFICATION EMISSION SOURCES

The Kosovo industrial complex is located in a large valley in the Kosovo Region of Yugoslavia and is surrounded by farming communities. The area has a climate similar to the Midwestern States in the U.S. and wind directions are predominantly from the north or south.

Five major operations are carried out within the industrial complex including coal gasification. These other operations are coal (lignite) mining, power and process steam generation with coal-fired boilers, manufacture of ammonia-based fertilizer, and coal preparation. A schematic diagram of the Kosovo industrial complex is shown in Figure 2-2. Since the coal preparation unit produces sized lignite for Lurgi gasification, it is considered part of the gasification plant.

All the operations in the Kosovo industrial complex, as well as the farming activities in the valley, are potential sources of atmospheric emissions. However, the emissions from coal gasification are expected to differ chemically from those attributed to the other sources listed above. Therefore, an analysis for specific pollutants and pollutant classes was carried out on the ambient aerosol samples collected around the industrial complex.

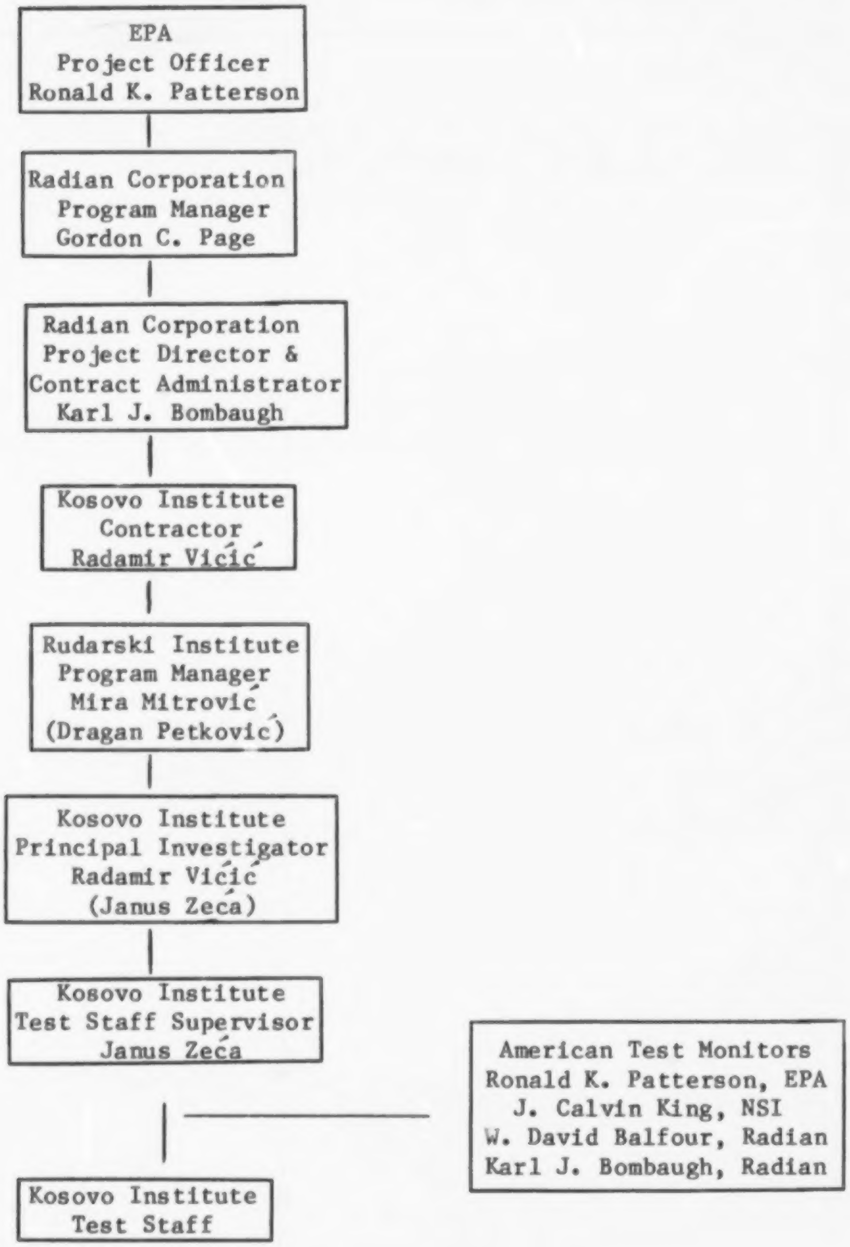

EPA
Project Officer
Ronald K. Patterson
Radian Corporation
Program Manager
Gordon C. Page
Radian Corporation
Project Director &
Contract Administrator
Karl J. Bombaugh
Kosovo Institute
Contractor
Radamir Vićić
Rudarski Institute
Program Manager
Mira Mitrović
(Dragan Petković)
Kosovo Institute
Principal Investigator
Radamir Vićić
(Janus Zeća)
Kosovo Institute
Test Staff Supervisor
Janus Zeća
American Test Monitors
Ronald K. Patterson, EPA
J. Calvin King, NSI
W. David Balfour, Radian
Karl J. Bombaugh, Radian
Kosovo Institute
Test Staff

Figure 2-1. Overall Project Organization for the Kosovo Air Sampling Program

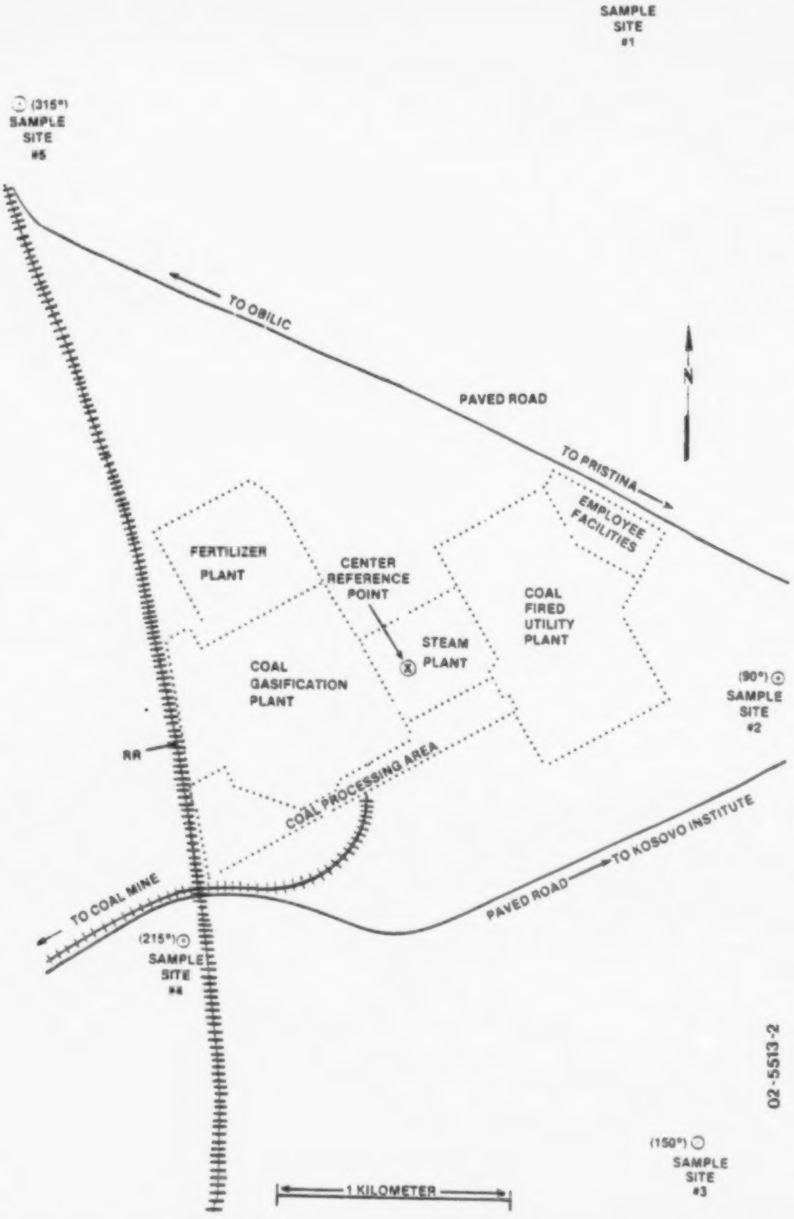

(15°)
SAMPLE SITE #1
(315°)
SAMPLE SITE #5
TO OBILIC
PAVED ROAD
N
TO PRISTINA
EMPLOYEE FACILITIES
FERTILIZER PLANT
CENTER REFERENCE POINT
COAL FIRED UTILITY PLANT
STEAM PLANT
COAL GASIFICATION PLANT
(90°)
SAMPLE SITE #2
RR
COAL PROCESSING AREA
TO KOSOVO INSTITUTE
TO COAL MINE
PAVED ROAD
(215°)
SAMPLE SITE #4
02-5513-2
(150°)
SAMPLE SITE #3
1 KILOMETER

Figure 2-2. Schematic of the Kosovo Complex with the Five Sampling Sites Indicated

2.1.1 Coal Gasification: Process Overview

The function of the coal gasification plant is to produce a medium-Btu gas (15 MJ or 3600 kcal/Nm^3) from lignite. This gas is used as fuel by surrounding industries and as a supply of hydrogen for the fertilizer plant. The gasification plant consists of eight unit processes:

- coal preparation (Fleissner process),
- coal gasification (Lurgi process),
- gas quenching/cooling,
- acid gas removal (Rectisol process),
- tar separation,
- phenol/NH_3 recovery (Phenosolvan process),
- by-product storage, and
- auxiliaries (flare, oxygen production, cooling tower, steam generation, process water treatment, etc.)

Figure 2-3 shows an overall plant flow scheme for the Kosovo gasification facility. This diagram also shows the major air, water, and solid waste streams associated with each operation in the plant.

Lignite is prepared in the Fleissner process by drying with high temperature steam and sizing to reject particles less than 6 mm or greater than 60 mm. The sized coal is reacted with oxygen and steam at 2.5 MPa (25 atm) pressure in Lurgi gasifiers to produce a raw medium-Btu gas. The raw gas is quenched and cooled to remove tars, oils, and phenols. In the Rectisol acid gas removal section, carbon dioxide and hydrogen sulfide are removed from the product gas. Tars and oils in the quench liquor are recovered in the Tar Separation Section and sent to storage. Phenols and ammonia are recovered from the quench liquor in the Phenosolvan process.

Each of the six Lurgi gasifiers is designed to convert 16 Mg/hr (17.6 tons/hr) into 12,500 Nm^3/hr (7100 scfm) of clean product gas. The design values for the gasification plant's inputs, products, and by-products are given in Table 2-1.

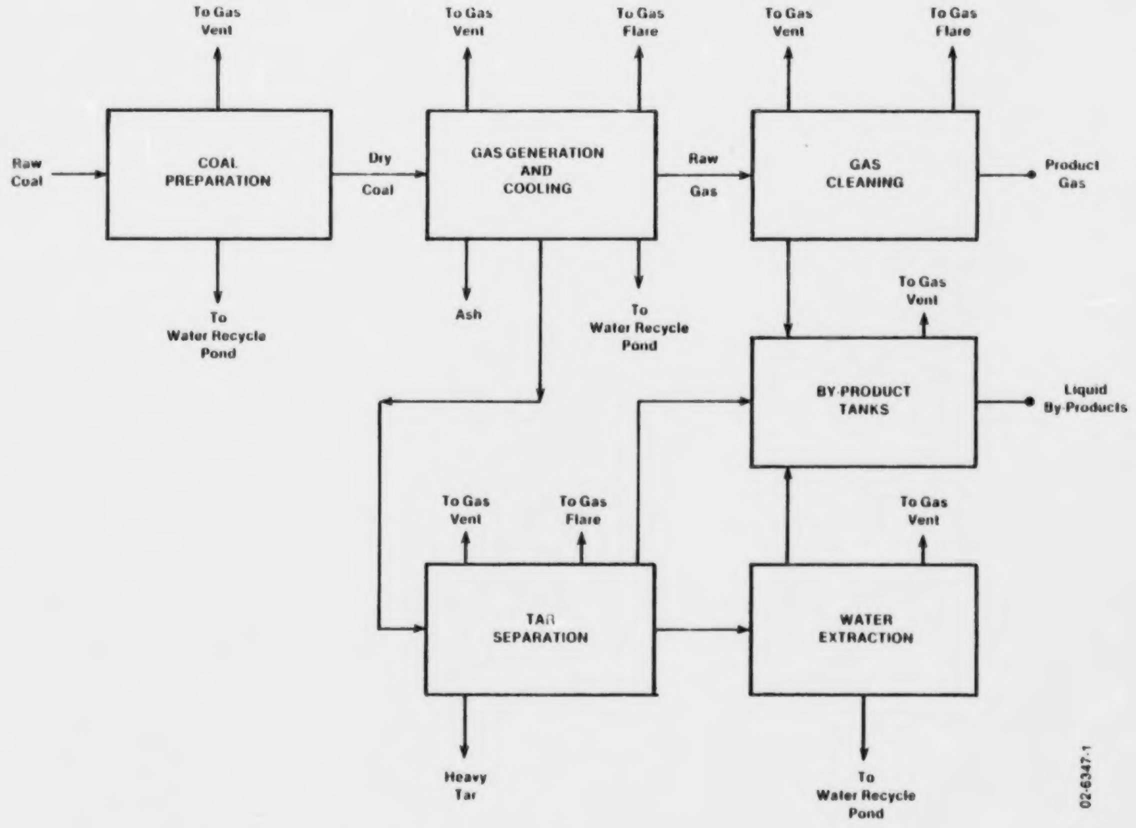

To Gas Vent
To Gas Vent
To Gas Flare
To Gas Vent
To Gas Flare
Raw Coal
COAL PREPARATION
Dry Coal
GAS GENERATION AND COOLING
Raw Gas
GAS CLEANING
Product Gas
To Water Recycle Pond
Ash
To Water Recycle Pond
To Gas Vent
BY-PRODUCT TANKS
Liquid By-Products
To Gas Vent
To Gas Flare
To Gas Vent
TAR SEPARATION
WATER EXTRACTION
Heavy Tar
To Water Recycle Pond
02-6347-1

Figure 2-3. Overall Flow Scheme of the Kosovo Lurgi Gasification Plant

TABLE 2-1. KOSOVO GASIFICATION PLANT DESIGN DATA

Inputs:	
Lignite Coal	80 Mg/hr
Steam	65 Mg/hr
Oxygen (96 Vol %)	9,900 Nm^3/hr
Outputs:	
Products:	
Clean Gas	60,000 Nm^3/hr
By-Products:	
Tar	2.2 Mg/hr
Oils	1.3 Mg/hr
Gasoline	0.65 Mg/hr
NH_4OH	0.96 Mg/hr
Crude Phenols	0.36 Mg/hr

NOTE: Data assumes 5 generators in service; one on standby.

2.1.2 Coal Gasification: Emission Sources

The gasifier emission sources and the general characteristics that differentiate them from other sources in the Kosovo industrial complex are summarized in this section. Table 2-2 is a summary of the emission sources in each section of the gasification plant. The emission streams generated in coal or lignite gasification contain the following mixture of substances:

- aromatic hydrocarbons and heterocyclics including benzene, toluene, xylenes, and possibly heavier organics such as PNA's,
- phenols and other oxygenated organics,
- sulfur species (H_2S, mercaptans, COS, thiophenes),
- nitrogen species (pyridines), and
- tar and oil aerosols.

These stream characteristics were used to design the analytical strategy for the ambient air samples collected around the Kosovo industrial complex.

2.2 LOCATION AND OPERATION OF THE SAMPLING SITES

2.2.1 Placement of Test Stations

Five sampling sites were established within one to two kilometers of the gasification facilities (Figure 2-2). Potential locations were considered based upon wind roses for the month of May, 1978. In May, the wind is predominantly from the North according to information furnished by Kosovo Institute, and based upon historical data.

The actual locations of the sites reflected the availability of the land (owner cooperation) and provisions for equipment security. The sites chosen allowed for collection of samples upwind and downwind of the gasifier to identify background levels of pollutants as well as downwind concentrations. The location of each of the sampling sites is shown in Figure 2-2 and are identified as follows:

Site #1: Raba's House
Site #2: Kosovo Institute
Site #3: Krusevac
Site #4: Train Station
Site #5: Kosovo B (Obilić)

TABLE 2-2. SUMMARY OF AIR EMISSION SOURCES FROM THE COAL GASIFICATION PLANT

Gasification Section Emission Source	Emission Source Characteristics
Fleissner Process:	
Coal Bunker Vent (1.1)	Coal Dust
Autoclave Vent (1.2)	Coal Dust, organics, sulfur species, nitrogen species
Condensate Tank Vent (1.4)	Organics, sulfur species, nitrogen species
Lurgi Gasification Process:	
Coal Bunker Vent (2.2)	Coal Dust
Coal Bucket Vent (3.1)	Coal dust & raw gas components (tars, oils, phenols, sulfur species, nitrogen species)
Low-Pressure Lock Vent (3.2)	
Quench Liquor Tank Vent (3.4)	Raw gas components
Ash Lock Vent (3.5)	Steam, ash dust
Rectisol Process:	
CO_2 Vent Gas (7.2)	CO_2, sulfur species, organics
Tar Separation:	
Tar Tank Vent (13.1)	Organics, sulfur species, nitrogen species, CO, phenols
Impure Tar Tank Vent (13.2)	
Medium Oil Tank Vent (13.3)	
Impure Medium Oil Tank Vent (13.4)	
Condensate Tank Vent (13.5)	
Phenolic Water Tank Vent (13.7)	

TABLE 2-2. (Continued)

Gasification Section Emission Source	Emission Source Characteristics
Phenosolvan:	
Cyclone Vent (14.1)	Organics, phenols, ammonia, sulfur species, nitrogen species, CO
Phenolic Water Tank Vent (14.2)	
Unclean Oil Tank Vent (14.3)	
Filtered Water Tank Vent (14.4)	
Degassing Column Vent (14.5)	
Ammonia Stripper Cooler Vent (14.6)	
Degassing Column Vent (14.7)	
Slop Tank Vent (14.8)	
Phenol Storage Tank Vent (14.9)	
DIPE Tank Vent (14.10)	
Ammonia Absorber Vent (14.12)	
Ammonia Storage Tank Vent (14.13)	
By-Product Storage:	
Tar Tank Vent (15.1)	Organics, sulfur species, nitrogen species, phenols
Medium Oil Tank Vent (15.2)	
Gasoline Tank Vent (15.3)	
Raw Phenol Tank Vent (15.4)	
Unclean Oil Tank Vent (15.5)	
NH_4OH Tank Vent (15.6)	
Flare:	Combustion products (CO_2, H_2O, SO_2, NO_x), organics, CO, tar, sulfur species, nitrogen species. Input streams to the flare (high pressure lock gases, H_2S-rich gas and tar separation expansion gas) contain tars, oils, sulfur species, nitrogen species, and other compounds found in the raw gas.

2.2.2 Location of Individual Sampling Sites

The distances are approximate and were measured from the approximate center (the steam tower in the steam plant) of the Kosovo complex (see Figure 2-2). The degrees indicated are the compass headings from this same reference point.

Site #1: Raba's House - Distance ∿2 km; Direction 15°

Site #1 was located about 35 m from a typical home. The factor with the most potential influenece on the local aerosols was a dirt road about 20 m predominantly upwind from the equipment. Other houses and gardens were scattered about the area. The power generator for the site and the gasifier were usually downwind of the sampling platform, about 40 m and 2 km, respectively. Other possible sources of aerosols and organic vapors resulted from the animal and human wastes (drainage) in the area, and the high level of domestic activity (children, pets, etc.).

Site #2: Kosovo Institute - Distance ∿1 km; Direction 90°

Site #2 was on the grounds of the Kosovo Institute. Specifically it was on the lawn behind the main building and there was little activity nearby. One possible source of contamination was the grill vent from the cooking area located about 40 m east northeast of the site. Another wing of the building was about 30 m distant. The paved road leading to the parking lot was about 80 m away. With the gasifier located due west, this site was usually not downwind from the plant.

Site #3: Krusevac - Distance ∿1.7 km; Direction 150°

Site #3 was located in a garden area behind a row of houses in an uncrowded, suburban village. There was a good deal of activity (children, pets, cars, etc.) in the vicinity. Both the row of houses at about 30 m and the dirt road at about 40 m were partially upwind of the site. Home heating effluent may have also been a potential source of particulate matter and volatile organics. A small ditch was about 2 m away and a low wall was 15 m to the east. Site #3 was typically 15-20 percent downwind.

Site #4: Train Station - Distance ∿1 km; Direction 215°

Site #4 was the principle downwind site (typically 40 percent) during the gasifier sampling period. The equipment was located in an open field normally used for grazing. However, several site specific features could have influenced the data. To the north were two coal conveyors, one fairly close (about 20 m) and one across a paved road (about 50 m). The road and the conveyors were about 7 m off the ground as they passed over the railroad track. The main railroad track passes about 30 m from the sampling site and carried 27 diesel and 21 steam locomotives daily. Across the paved road was a single track for an electric coal transport train running between the mine and the coal processing area. The gasifier plant was located to the northeast (predominantly upwind from Site #4), and the site electrical generator was located about 40 m downwind of the sampling equipment, generally to the southwest. This site was most subject to contamination from local factors of the five sites.

Site #5: Kosovo B - Distance ∿2 km, Direction 315°

Site #5 was on the outskirts of a small village. The major influences in this rather pastoral setting were due to either cars and carts on a dirt road about 100 m distant, heavy vehicular traffic on the main paved road (to Obilic) several hundred meters away, or the railroad just beyond the road. This was the most remote of the five sites; even the nearest house was about 100 m away.

2.2.3 Description of Sampling Equipment

The sampling equipment used at each site (see Table 2-3) included:

- a HiVol aerosol sampler with an organic vapor trap,
- a time-phased aerosol sampler (streaker) mounted on the HiVol sampler,
- a Battelle-type single-jet cascade impactor, and
- a LoVol aerosol sampler.

Electric power was provided at each of the sampling stations by a portable, gasoline-powered generator (Sears, 3 kw). The generator was placed about 40 m downwind.

Meteorological Support

Meteorological support stations used during the field study were placed at two of the sites (#3 and #5) to provide information about the wind direction and speed and other meteorological parameters. A Climatronics station placed at Site #5 (predominantly upwind) provided a continuous record of:

- wind speed,
- wind direction,
- ambient temperature,
- barometric pressure, and
- total solar radiation.

Data was recorded both on strip chart and magnetic tape (Datel Data Logger II).

TABLE 2-3. SUMMARY OF SAMPLING EQUIPMENT

Equipment Item	Collection Media	Sample Collection	Nominal Volume	Flow Rate	Sampling Period
High Volume Sampler (HiVol)	Gelman Microquartz Filters	TSP*	1500 m^3	1 m^3/min	24 hrs
Organic Vapor Trap	Tenax GC Resin	Volatile Organics	6 m^3	4 L/min	24 hrs
Time-Phased Sampler (Streaker)	Nuclepore Polycarbonate Filter	Particles (<15 μm)	--	∿1 L/min	Continuous
Cascade Impactor (Battelle)	Coated Mylar Surfaces (Nuclepore Back-Up)	Particles (5 stages between 4.0-0.25 μm)	0.36 m^3	∿1 L/min	6 hrs
Low Volume Aerosol Sampler (LoVol)	Gelman Microquartz Filters	Particles (<15 μm and <2.0 μm)	11 m^3	∿30 L/min	6 hrs

*TSP = Total Suspended Particulate matter (<100 μm).

A Bendix Aerovane was placed at Site 3. This unit provided continuous wind speed and wind direction on strip chart only. Due to the failure of an automatic dew point sensor in the station, it was necessary to make wet bulb-dry bulb temperature measurements at six hour intervals at Kosovo Institute (Site #2) by the laboratory personnel. This data was reduced to values of ambient relative humidity.

2.3 SAMPLE COLLECTION AND HANDLING

2.3.1 Sampling Program

The sampling program was organized as shown in Figure 2-1. American supervisors instructed the Yugoslav personnel in sample collection technologies during a series of training sessions. This allowed the Yugoslavs to carry out many of the tasks involved in the daily servicing of the sites. An American representative supervised each of the three shifts. Each of the shifts had specific tasks (Table 2-4) which were outlined for them as a daily schedule. The morning and afternoon shift included personnel who performed the necessary weighing, media preparation, sample logging, and sample packaging tasks in addition to the servicing of the sites. The American shift supervisors provided written daily status reports to Radian's representative coordinator. These status reports, along with any other problems or requests, were presented at daily planning meetings so that immediate action could be taken. Information was relayed to the varous shifts via a message board.

Quality control of the daily logged samples and field records was performed during a two hour period following shift A but before shift B personnel had reported to work. This schedule allowed the quality assurance program to be accomplished without disrupting the collection of samples.

2.3.2 Training Session and Scheduling

The bulk of the site maintenance was carried out by the Yugoslavs. In order that they fully understood their duties and the importance of their tasks, efforts were made to educate them in the proper procedures and the reasons for those procedures. A detailed Field Operations Manual was provided by EPA and translated ahead of time. Upon arrival of the U.S. team, workshops were held covering all procedures, techniques, records, and the theory of operation. In addition, the part that each measurement and each worker played in the overall project was stressed, as was the necessity and function of the quality assurance personnel.

TABLE 2-4. SPECIFIC TASKS PERFORMED DURING EACH SHIFT

	Hours	
A Shift (4 Yugoslavs)	(0600-1400)	● 0600 hr servicing of Sites #2, #3, #4 ● obtain gasoline and fill generators ● 1200 hr servicing of all sites ● check streaker flow rates and change slides as needed ● LoVol filter weighings ● sampling media preparation ● sample logging ● sample packaging and storage ● wet bulb-dry bulb measurement
	Hours	
B Shift (3 Yugoslavs)	(1600-2400)	● 1800 hr servicing of all sites ● obtain gasoline and fill generators ● service meteorological stations ● 2400 hr servicing of Sites #1 and #5 ● sampling media preparation ● sample logging ● sample packaging and storage ● wet bulb-dry bulb measurement
	Hours	
C Shift (2 Yugoslavs)	(2200-0600)	● 2400 hr servicing of Sites #2, #3, #4 ● flow measurement for HiVol ● 0600 hr servicing of Sites #1 and #5

The U.S. team set up and calibrated the sampling apparatus at each site. They prepared a detailed list of site servicing duties (in Serbo-Croatian) along with field data collection sheets, log records, and quality assurance forms. Shift specific duties were detailed. Radian personnel were responsible for collecting all sample blanks prior to and immediately following the sample period.

On Thursday, May 10, 1979, the training sessions began. Eleven Yugoslavians were designated for work on the project. Detailed instructions about all phases of their involvement were given. All filter samples were to be prepared in the lab, taken to the field site, loaded, run, unloaded and returned to the lab where they were logged and packed. The LoVol filters were the only ones weighed in the Kosovo labs. They were allowed 24 hours to equilibrate before initial weighing. The filters were then logged and packed for delivery to the field. Upon return they were equilibrated, reweighed, recorded and packed. U.S. personnel oversaw all operations, but the Yugoslavs did the actual handling. Daily quality assurance weighings were also performed on a metal ferrule (for constant weight) and two blank filters to test effects of temperature, humidity and pressure. Also, 10 percent of all filters were routinely reweighed as a quality assurance procedure.

The teams which would do the actual site servicing in the field were taken to the sites and instructed in all the proper procedures and techniques. The vital importance of these tasks was stressed. Each team was given "hands on" training. Shifts were also instructed in power generator maintenance and told to move them downwind of the sampling station if necessary.

Finally, the importance of record keeping and logging was reemphasized. Examples of all forms used in the operation were included in the Field Operations Manual in both English and Serbo-Croation. Testing began at 0000 hours on Monday, May 14, 1979.

2.3.3 Sample Collection

The maintenance and servicing of each site was carried out by Yugoslavian personnel. Each site was checked at least every six hours. HiVol and vapor trap samplers were changed every 24 hours (at approximatey 2400 hours). LoVol samplers and the Battelle impactors were changed every six hours. The particulate streaker sampler and the meteorological station were checked during each visit and serviced when needed. U.S. personnel acted as supervisors and consultants on each site visit. The quality assurance procedures were either carried out by U.S. personnel directly or at their direction. Before the sampling began, training sessions culminated in a two day dry run under Radian's supervision. The Field Operations Manual included a section on laboratory procedures, prepared by Radian, and covered weighing of the filters and loading and unloading the Battelle Cascade Impactor.

HiVol/Vapor Trap--At the end of a sampling period (every 24 hours) the 265 mm Gelman microquartz filter was carefully removed and placed in its original, numbered, aluminum foil package. Another clean filter was put in place. All operations were carried out using forceps and gloves. The Tenax organic vapor trap was also carefully removed and sealed with end caps before fresh traps were mounted.

Flow rates for both the HiVol filter system and the Tenax columns were checked, recorded (prior to change-out), and adjusted to the desired rate after start-up. The filter and Tenax samples were subsequently returned to Kosovo Institute for packaging. Field data and logging information were recorded on appropriate forms.

Streaker Sampler--At each visit the maintenance personnel recorded the streaker sampler flow rate and vacuum gauge reading and checked the sampler for continued movement or any abnormality. When the collection slide was changed (every seven days), the appropriate sample numbers were recorded. The flow rate was checked daily with a Kurz Model 341 mass flow meter (furnished by EPA) and recorded on the appropriate form.

Battelle Cascade Impactor--The flow through the particle sizing impactor was checked and recorded before the device was removed from its stand. The entire impactor was removed for transport back to the lab, a freshly loaded impactor was installed in its place and its initial flow was recorded. At the plant laboratory, the five stage substrates and the back-up filter were carefully removed and placed in their respective, sequentially numbered vials for shipment. The impactor was then cleaned and reloaded.

LoVol Filters--At every sixth hour during the sampling period, the LoVol filters were changed. The initial and final flow rates were recorded. The exposed filter was carefully removed (with forceps) and placed in its numbered petri dish. A clean filter was transferred from its petri dish to the Gelman filter holder. The holder was then positioned correctly and the flow rate was adjusted, if necessary. The second of the two filters was changed in a similar manner.

The exposed LoVol filters were reweighed at the Kosovo Institute laboratory. Prior to all weighings, the filter was equilibrated to laboratory conditions for 24 hours. The filter was then replaced in its petri dish and delivered to Radian personnel.

Meteorological Station--At each visit to Site #3 (every six hours), the Bendix Aerovane and strip chart recorder were inspected and their correct operation was verified. The time and date were recorded on the chart (this is also recorded automatically). At each visit to Site #5 (every six hours) the Climatronics station was checked, and the batteries were tested and operation of the Datel Data Logger II was verified. Any abnormalities were reported to and corrected by the Northrup electronics specialist on-site.

Electric Generator--The gasoline powered generator was routinely checked each six hours for overload, oil, etc., and the tank was refilled. All inspections and information were recorded on a designated form.

Laboratory Functions--The laboratory personnel measured and recorded the temperature and humidity during each six hour interval. They were also responsible for the initial and final weighings of the LoVol filters, sample media preparation, and sample logging and packaging.

Supervision and Consultation--In addition to organizing the sampling procedures and schedule, Radian personnel were on-site continuously to supervise the operation and provide consultative services. They performed quality assurance spot checks of weighings, data logging, and auditing of all flows. They also observed the Kosovo Institute personnel in the performance of their site maintenance duties and verified that schedules were being met.

The Radian personnel were responsible for the proper functioning of the collection equipment, including all start-up and shut-down procedures. They also held custody of all collected samples, including the LoVol filters after final weighing by the Kosovo Institute personnel. As part of their quality assurance program, notations were made of daily weather conditions, plume behavior, irregularities in any procedures, etc. The results of the quantitative quality assurance procedures are described in the following sections.

2.3.4 Sampling Quality Assurance

Throughout the sampling period efforts were made to monitor and insure the quality of the data. This vital task was carried out by Radian personnel before, during and after the actual sampling. The purpose was to detect and correct improper procedures and to provide a means of evaluating the accuracy of the data.

Assurance Procedures Prior to Sampling--Since the bulk of the samples were to be collected by Yugoslavians at the site, a Field Operations Manual was prepared, translated, and given to the sampling personnel so that they could familiarize themselves with the operation of the equipment. The sampling equipment was assembled at the designated sites and tested for operability. A Mettler Model ME 30/36 Electronic Microbalance was set up at the Kosovo Laboratories by the EPA representative and calibrated for use.

Flow Audits--Since all of the atmospheric measurements involved sampling a volume of air, an accurate reading of the volume that was sampled was essential. In the course of the sampling, readings on all instruments were spot checked daily by Radian personnel using a Kurz Model 543 portable flow calibration kit. All differences over 5 percent were noted on the flow audit log sheets and the cause of the discrepancy was resolved. Differences over 5 percent occurred about 20 percent of the time.

Weighing Audits--LoVol sample filters were weighed at the Kosovo Laboratories on a Mettler Microbalance. Daily weights were recorded for standard objects (a metal object and two blank filters) to guard against instrument drift or changes due to humidity, temperature, and pressure. All samples were allowed at least 24 hours to equilibrate to laboratory conditions before weighing.

From time to time, filters which had been weighed by Rudarski or Kosovo Institute personnel were selected at random and reweighed by Radian scientists. Ten percent of all filters were routinely reweighed daily by the Yugoslavian technicians performing the weighings.

Other Assurance Procedures--Daily quality control logs were maintained. These logs were checklists to insure that all the forms had been filled out and all the proper procedures were followed each day. They also included the total number of samples logged each day, the number screened (reweighed) for quality control, and a corresponding number of field data forms. Procedural interrupts, malfunctions, etc., were noted on these sheets.

At the completion of the sampling effort, all the samples were carefully packed and sealed under the inspection of Radian personnel. Upon arrival at Radian's Austin location, the packaging of the samples was inspected and no evidence of tampering was found.

2.3.5 Sample Distribution

The sampling period consisted of 16 consecutive days. At the end of this period, all samples were given to the U.S. team along with copies of all data sheets; originals were kept at the Kosovo Institute. Original quality assurance logs were kept by Radian personnel. The samples were then distributed to various members of the entire project team (see Table 2-5). All the samples from Days 1-4 and 13-16 were delivered to INEP in Belgrade. The samples from the middle eight days (5-12) were transported to the U.S. (to Radian labs in Austin, Texas) where they were further distributed as follows: days 9-12 of HiVol and Tenax vapor traps to Oak Ridge National Laboratory for organic analysis (mainly extractions, GC and GCMS); all impactor and streaker samples to Florida State University for multi-element analysis (by PIXE); three grab sample bombs to EPA/RTP. Radian retained the remaining samples; days 5-8 of HiVol filters and Tenax vapor traps and days 5-12 LoVol filters.

TABLE 2-5. SAMPLES COLLECTED AND RESPECTIVE RECIPIENTS

Organization	HiVol Filters	Organic Vapor Traps	Battelle Impactor Disc Sets	Streaker Sampler Slides	LoVol Filters	Grab Sample Bombs
INEP[1]	42	83	157	6	316	3
Radian/OGC[2]	23	42			326	
ORNL	22	42				
Florida State University			161	12		
EPA/GKPB[3]						3
TOTALS	87	167	318	18	642	6

[1] INEP - Institut za Primenu Nuklearne Energije, Belgrade, Yugoslavia.

[2] The Oregon Graduate Center (OGC) received two sections of each LoVol filter for carbon speciation, Radian analyzed for specific water soluble ions and 15 metallic elements.

[3] GKPB - Gas Kinetics and Photochemistry Branch, Environmental Sciences and Research Laboratory, North Carolina.

SECTION 3.0

ANALYTICAL METHODS

At the end of the sampling period, all samples were in the custody of Radian personnel at the Kosovo site. In accordance with prior agreement, one-half of all the samples were delivered to INEP in Belgrade and one-half were returned to Radian's laboratory in Austin, Texas. This section details the analytical methods that were used on the samples delivered to Radian.

3.1 TREATMENT OF METEOROLOGICAL DATA

The meteorological data collected on-site were reduced to engineering units for 2-, 6- and 24-hour time segments by EPA and the results provided to Radian. In addition to the average temperature and pressure over the period, digitalized wind speed (in 5 km/hr segments) and direction (given as blowing from one of eight compass points) were given.

One of the principle methods used to determine the contribution of the gasifier to observed conditions was to compare the concentration of a species upwind and downwind of the facility. Thus it was necessary to use the wind speed and directional data to determine the percentage of time that each site was "downwind" of the facility during each sampling period. The details and results of the calculations are given in Section 4.1.

In addition to the percent downwind tables, observations of weather conditions were included along with the data. These observations were the only account of vertical diffusion or convection patterns, since the meteorological station had no facility for vertical wind flows or temperature profiles.

3.2 PHYSICAL ANALYSIS OF PARTICULATE MATERIAL

This section deals with the physical analysis of the particulate samples. The principal procedure was determination of mass concentration, or loadings. Each of the LoVol filter catches, fine and total, was weighed (filter substrates were tared). The LoVol loadings were plotted against the percent downwind and trends sought. Where a trend appeared to exist, a regression analysis was performed.

After the mass loadings were recorded, the particle-laden filters were cut up for distribution and chemical analysis. The cut-outs were precisely measured circular discs (see Figure 3-1). Each filter provided four discs as shown; they were distributed for the various analyses discussed in Section 3.3. The remaining filter was used for ICAP trace element analysis. Under visual inspections, deposition appeared uniform but uniform loading was never verified quantitatively.

Selected filters were prepared for the scanning electron microscope. That is, small cut-outs were mounted on platforms and sputtered with gold. Various combinations of upwind, downwind, <15 μm catch, and <2 μm catch were viewed and photographed.

3.3 INORGANIC ANALYTICAL METHODS

Precisely measured circular discs were cut from the LoVol filters (Gelman Microquartz) as shown in Figure 3-1. Thus, assuming uniform loading, the amount of a species on a piece of filter could be measured and related back to the total amount on the filter (see Section 3.2). Various elemental and chemical analyses were carried out on these segments.

3.3.1 Elemental Analyses

Elemental analyses performed on the LoVol, streaker, and the impactor aerosol samples were as follows:

- ICAP - Inductively Coupled Argon Plasma emission spectroscopy is capable of simultaneous measurement of multiple elemental concentrations. The filter substrates were digested in a concentrated HF and HNO_3 solution and injected into the ICAP. A similar procedure was followed for blank filters. The output is fully automated.

- PIXE - Proton Induced X-Ray Emission spectroscopy was used for the multi-element analysis of the inertial impactor substrates and the streaker sampler filters (Florida State University).

- H,C,N,S - Hydrogen, Carbon, Nitrogen, and Sulfur were analyzed in a graphite furnace by Huffman Laboratories, Inc. (Wheatridge, Colorado). The filter segments were vaporized directly, and no other preparations were necessary.

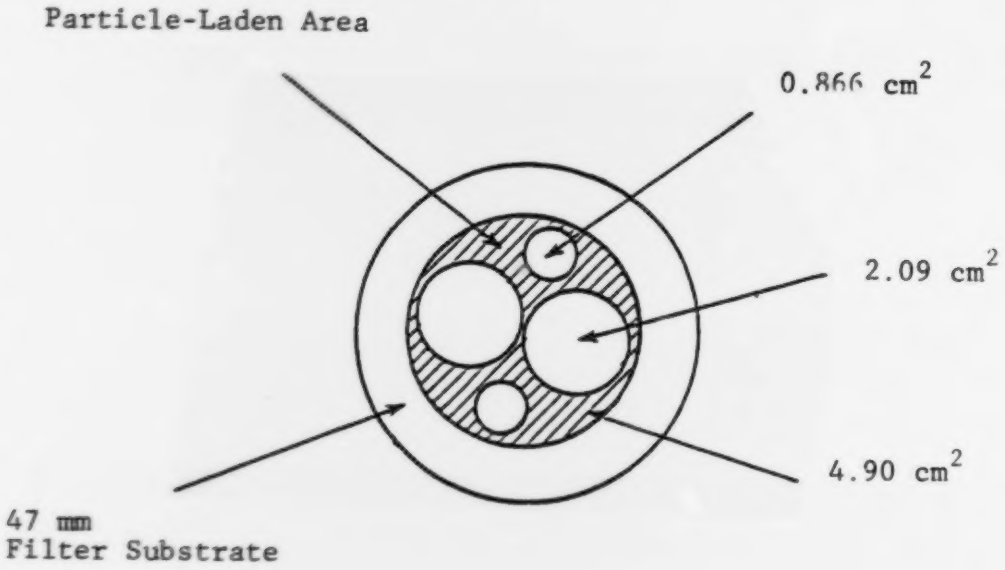

Particle-Laden Area
0.866 cm^2
2.09 cm^2
4.90 cm^2
47 mm
Filter Substrate

Figure 3-1. Cut-Out Patterns for Particle-Laden Filters from the LoVol Samplers

3.3.2 Chemical Analyses

Chemical analyses performed on the LoVol aerosol samples were:

- IC - Ion Chromatography was used to analyze the water soluble extract of the LoVol filters for Na^+, NH_4^+, NO_3^-, $SO_4^=$, and Cl^-. Essentially all Na^+, NH_4^+, and NO_3^- compounds are soluble and dissolution of these species should be complete. Most sulfates and chlorides are also soluble and should be completely dissolved. No attempt was made to analyze the leached filter and aerosol residue for sulfate or other species; however, the procedure, as described below, is recognized to be highly efficient.

  Segments from the filter were immersed in a known volume of hot deionized water and agitated for four hours. An additional four hours was allowed for undissolved particles to settle before an aliquot was taken for analysis. A Dionex ion chromatograph was used with a separate column for cations and anions and a conductivity cell detection system. Filter blanks were run, and the average blank values subtracted from the sample filters.

- Carbon Speciation - Certain samples, selected by Radian as representative of upwind/downwind pairs, were sent to the Oregon Graduate Center. They were analyzed for major carbon species such as total carbon, graphite, carbonate, organic, etc.

3.3.3 Quality Assurance

As standard procedure, blank filter segments were run through the identical analyses as the exposed filters, and the results were incorporated as differences. In addition, NBS standard reference material #1648 (urban particulate matter) was included as a blind sample in the ion chromatography and CHNS analyses. In the ion chromatography, duplicate runs of ten percent of the filters were made routinely; differences generally were small (<20%), but occasionally larger differences (<50%) were noted, particularly for sulfate. In the case of sulfate, with 64 runs made, eight duplicates were analyzed. Two of these differed by just over 50 percent , but the absolute values were so small that the percentage difference was distorted. One duplicate varied by 43 percent. The other five agreed within 20 percent, with three agreeing within 6 percent.

3.4 ORGANIC ANALYSIS METHODS

The objectives of Radian's program in the trace organic analysis of the Kosovo aerosol samples were threefold:

- qualitative and quantitative characterization of the potentially harmful organic compounds in the aerosol samples,
- validation of this characterization in a program of analytical quality assurance (QA), and
- relation of the organic characterization of the atmospheric aerosol to the GC profile of the emissions of the coal gasification facility.

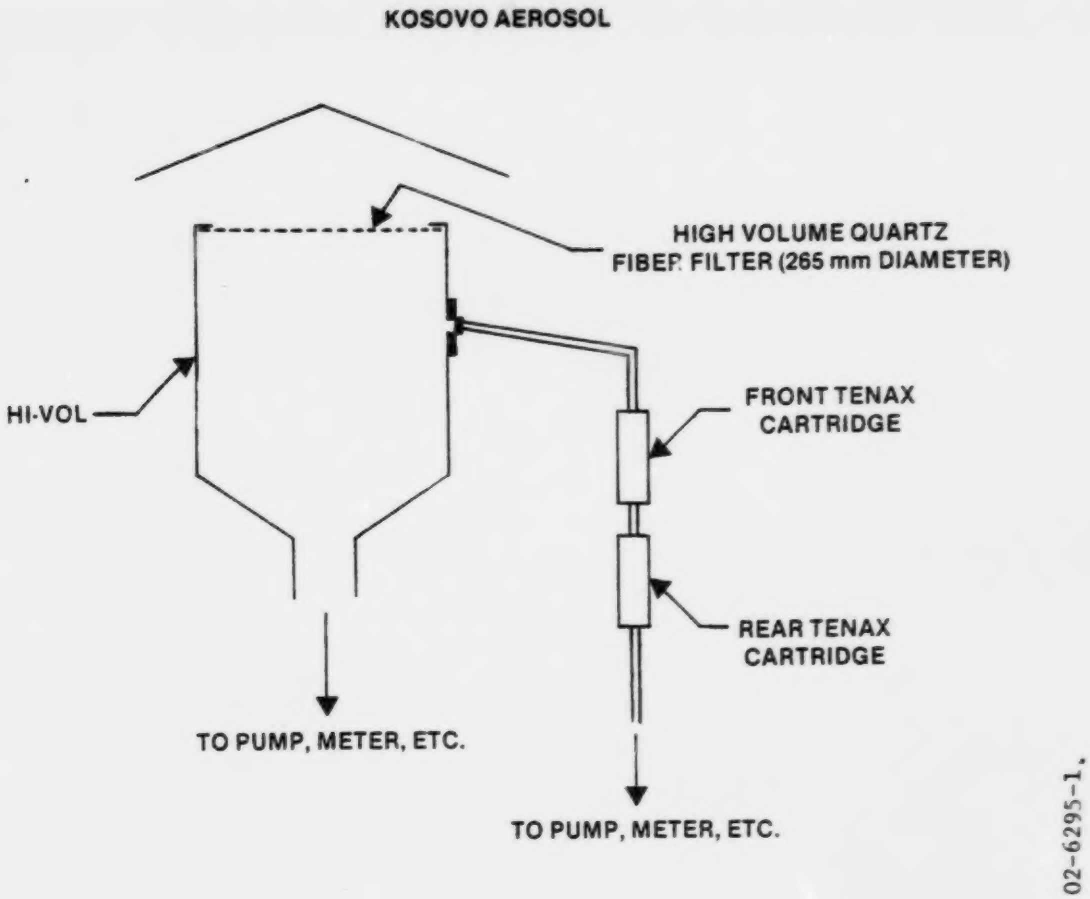
The strategy and methods used to achieve these three objectives are described in the sections to follow.

3.4.1 Organic Analysis Strategy

The sampling configuration for collecting particulate matter and vapors for subsequent organic analysis is shown in Figure 3-2. A photograph of one of the Tenax vapor trap cartridges prepared by the Oak Ridge National Laboratory for this program is shown in Figure 3-3. The samples distributed to Radian consisted of the sets collected over four days (days 5-8) at each of five sites surrounding the Kosovo industrial complex. Each 24-hour sample set for organic analysis consisted of the particle catch on a high volume (HiVol) microquartz fiber filter and the adsorbed organic vapors on two Tenax resin cartridges. The two Tenax cartridges were in series and downstream from the HiVol filter, sampling $\sim 1/250$ of the air passing through the filter.

The organic analysis strategy devised by Radian included:

- development and validation of methods for trace organic analysis of the Kosovo atmospheric samples paralleling those in use by the other EPA contractors and INEP;
- development of a step-wise approach to an overall characterization of the organic components in the emissions from the Kosovo-Lurgi gasification plant. The steps were:
  - Screening (prioritize samples and screen by GC/FID)
  - Profiling (qualitative and semi-quantitative analysis of samples and gasification by-products)
  - Verification (use of standard compounds to confirm identification and yield a better quantitation of compound concentrations)


KOSOVO AEROSOL
HIGH VOLUME QUARTZ FIBER FILTER (265 mm DIAMETER)
HI-VOL
FRONT TENAX CARTRIDGE
REAR TENAX CARTRIDGE
TO PUMP, METER, ETC.
TO PUMP, METER, ETC.
02-6295-1.

Typical parameters for organic aerosol sampling:

Sample rate ≅ 1 m^3/min

Sample volume ≅ 1400 m^3/24 hr

Typical parameters for organic vapor sampling:

Sample rate ≅ 4 liters AIR/min

Sample volume ≅ 5.8 m^3/24 hr

Figure 3-2. Configuration and Parameters for Collecting Aerosol Samples for Organic Analysis

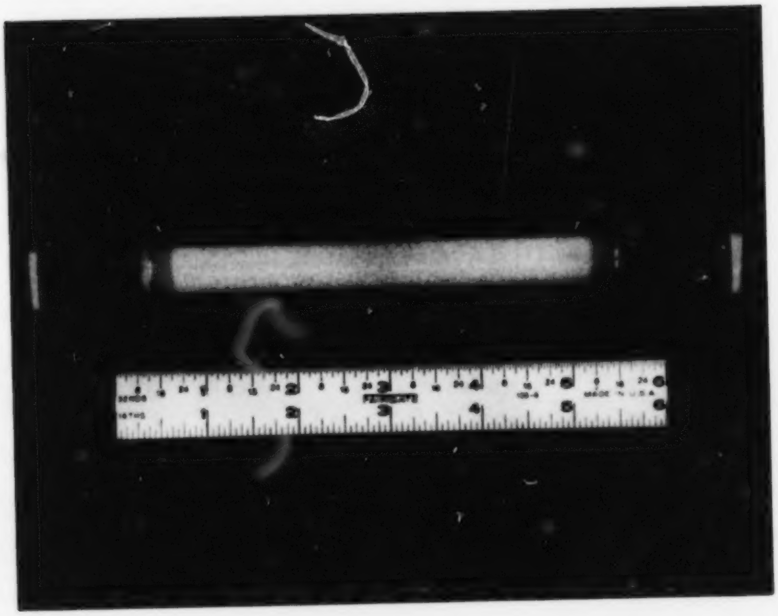


Figure 3-3. Photograph of a Tenax Vapor Trap Used in the Kosovo Aerosol Sampling

- comparison of the gasification plant's organic emissions with the compounds in its by-products and the appropriate compound AMEG concentration goals for monitoring health effects.

The elements of Radian's program in QA and organic analysis are summarized in Table 3-1. An overview of the multiple separation and analysis techniques employed for the gasification plant ambient air samples is shown in Figure 3-4. A detailed analytical flow diagram for screening the Tenax resin samples is given in Figure 3-5 while that for the profiling analyses is shown in Figure 3-6. The detailed analytical scheme for the treatment of the HiVol filters is given in Figure 3-7.

In accord with the QA program objectives and the analytical strategy presented in Figures 3-4 through 3-7, a detailed work plan was developed. A series of experiments and measurements directed toward methods development and validation are delineated in Table 3-2. A matrix of selected samples and analytical methods for screening and characterization is shown in Table 3-3. The methods for preparation and analysis of samples and standards are described in detail in the following sections. The results of methods validation and QA are presented in Section 4.

3.4.2 Sample Preparation and Separations

Prioritization of Aerosol Samples by Site

It was judged that the objectives of the organic analysis QA would be served best by focusing attention on a prioritized group of samples, selected by sampling site. The basis for this selection is the choice of a set of sites representing as nearly as possible the range: 0-50-100 percent downwind from the gasification plant.

For the sampling sites surrounding the gasifier facility at Kosovo, the selection for prioritization was as follows:

Site #1: 2 km NNE from the facility, showed an average 24-hour composite percent downwind value of typically approximately 1 percent for Days 5, 6, and 7, and approximately 10 percent for Day 8; this site is termed the "upwind" site;

Site #4: 1.25 km SW from the facility, exhibited the highest average 24-hour composite percent downwind values, typically approximately 40 percent for Days 5, 6, and 7 and approximately 20 percent for Day 8; this site is called the "downwind" site;

Site #3: 1.75 km SE of the gasifier, regularly showed an approximate 20 percent downwind value and was thus intermediate between Sites #1 and #4.

TABLE 3-1. ELEMENTS INCORPORATED IN RADIAN'S PROGRAM OF ORGANIC ANALYSIS AND QUALITY ASSURANCE

1. A step-wise approach with prioritization and initial screening of all samples proposed for detailed analysis.

2. Homogenization and aliquotting of the Tenax sorbent resin for multiple, replicate analyses.

3. Solvent extraction of the particulate matter caught on the HiVol filter; recovery of the organic vapor species sorbed on the Tenax by two independent methods: solvent extraction and thermal desorption.

4. Dosing of the Tenax resin and HiVol filters prior to extraction/analysis with deuterated aromatic compounds to serve as internal standards for recovery.

5. Analysis by gas chromatography to quantitate the breakthrough, recovery and concentrations of major organic species in the air samples.

6. Chemical speciation of the organic components in the ambient samples by gas chromatography-mass spectrometry (GCMS) and by specific chromatographic detectors selective for sulfur- and nitrogen-containing species.

7. Correlation of the observed air contamination results with the concurrent analytical results of the by-products of the coal gasification facility such as gasoline, middle oil and tar.

8. Comparison of measured organic compound concentrations in the Kosovo atmospheric samples with the corresponding AMEG values for monitoring health effects.

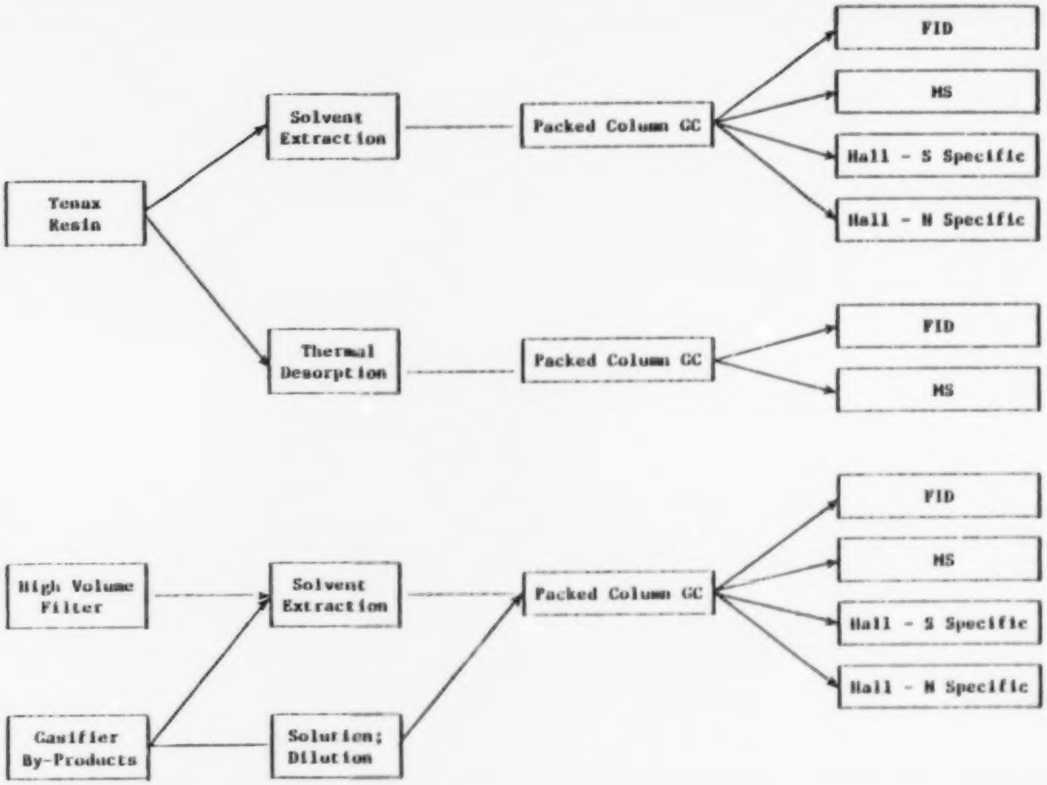

FID
MS
Solvent Extraction
Packed Column GC
Hall - S Specific
Tenax Resin
Hall - N Specific
FID
Thermal Desorption
Packed Column GC
MS
FID
MS
High Volume Filter
Solvent Extraction
Packed Column GC
Hall - S Specific
Hall - N Specific
Gasifier By-Products
Solution; Dilution

Figure 3-4. Schematic Diagram of the Multiple Separation and Analysis Methods Used for Ambient Aerosol Samples and Gasifier By-Product Characterization

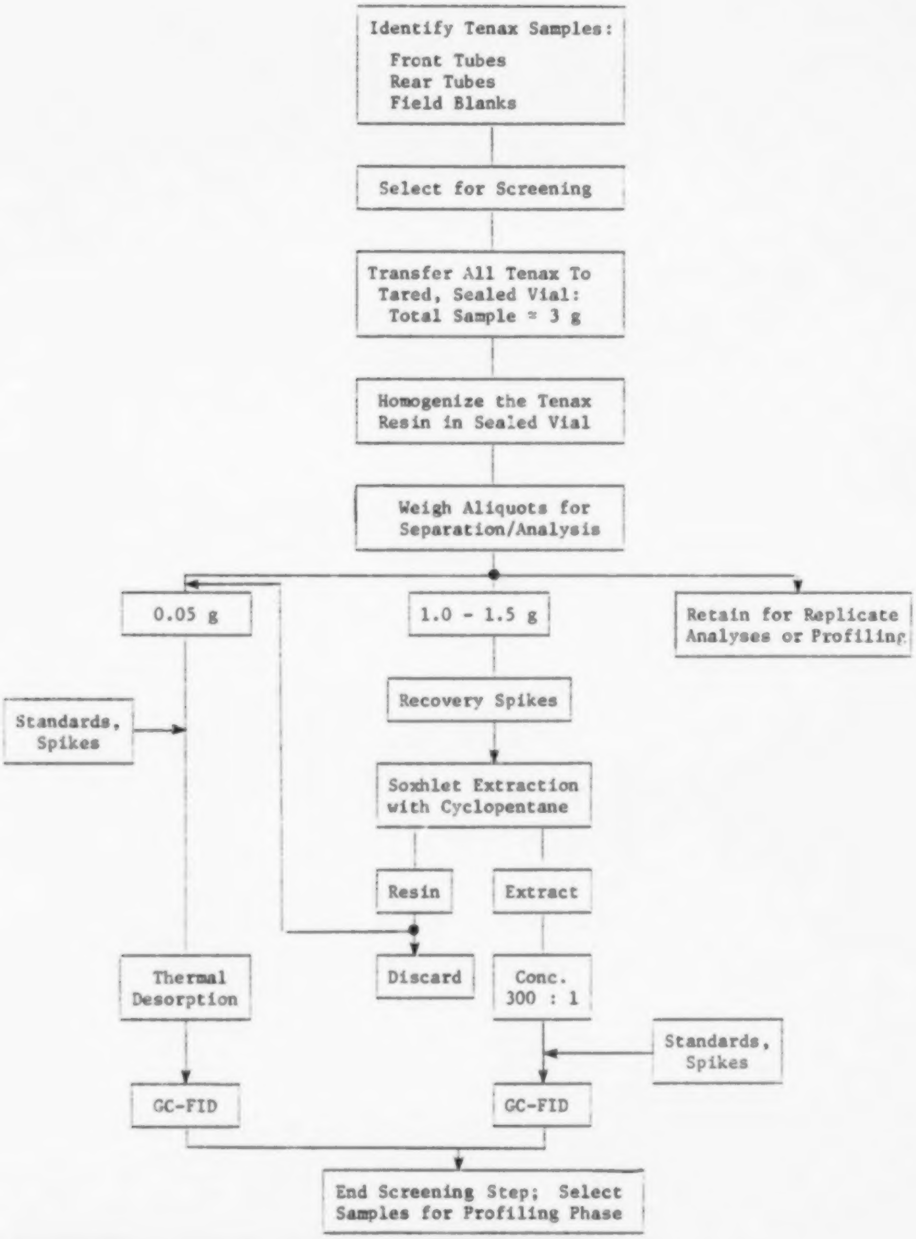

Identify Tenax Samples:
Front Tubes
Rear Tubes
Field Blanks
Select for Screening
Transfer All Tenax To Tared, Sealed Vial: Total Sample ≈ 3 g
Homogenize the Tenax Resin in Sealed Vial
Weigh Aliquots for Separation/Analysis
0.05 g
1.0 - 1.5 g
Retain for Replicate Analyses or Profiling
Standards, Spikes
Recovery Spikes
Soxhlet Extraction with Cyclopentane
Resin
Extract
Thermal Desorption
Discard
Conc. 300 : 1
Standards, Spikes
GC-FID
GC-FID
End Screening Step; Select Samples for Profiling Phase

Figure 3-5. Analytical Flow Diagram for Tenax Resin Screening

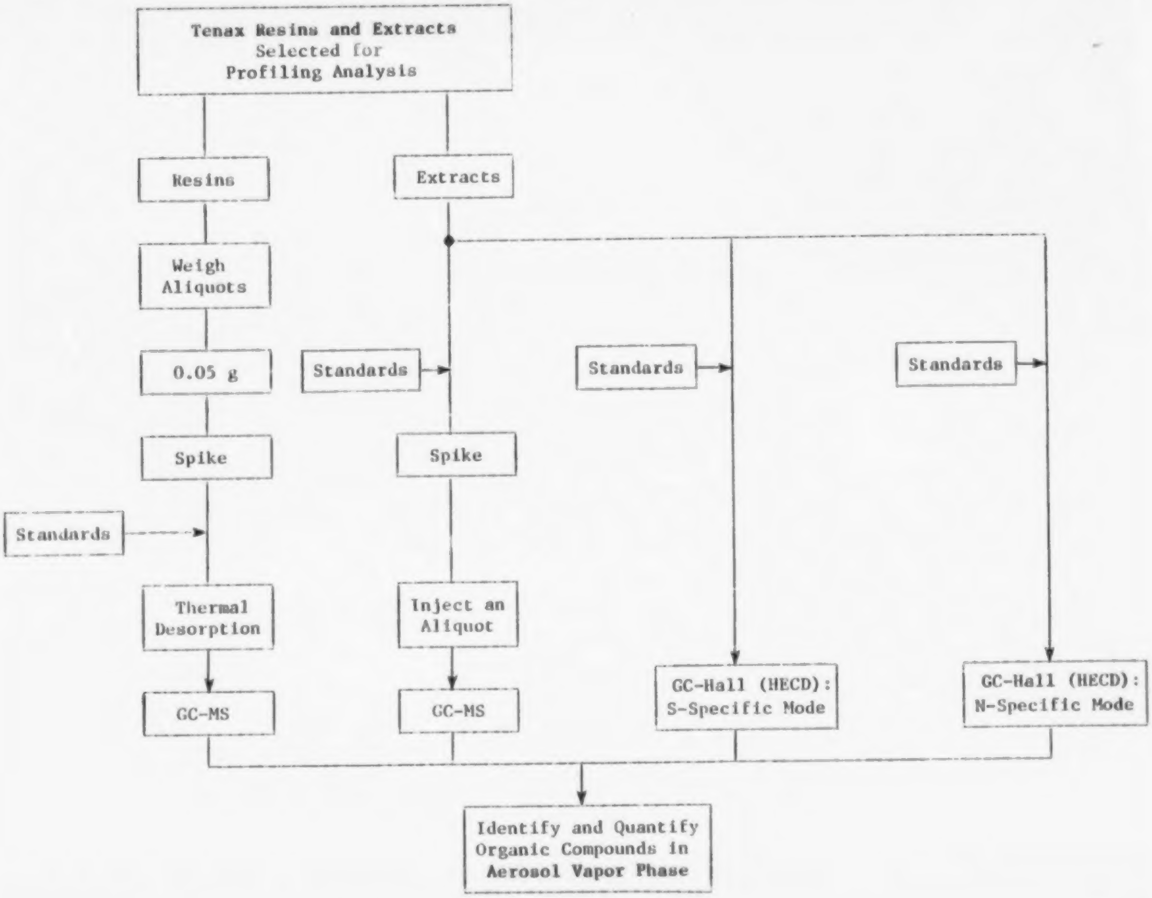

Tenax Resins and Extracts Selected for Profiling Analysis
Resins
Extracts
Weigh Aliquots
0.05 g
Standards
Standards
Standards
Spike
Spike
Standards
Thermal Desorption
Inject an Aliquot
GC-MS
GC-MS
GC-Hall (HECD): S-Specific Mode
GC-Hall (HECD): N-Specific Mode
Identify and Quantify Organic Compounds in Aerosol Vapor Phase

Figure 3-6. Analytical Flow Diagram for Tenax Resin Profiling Analyses

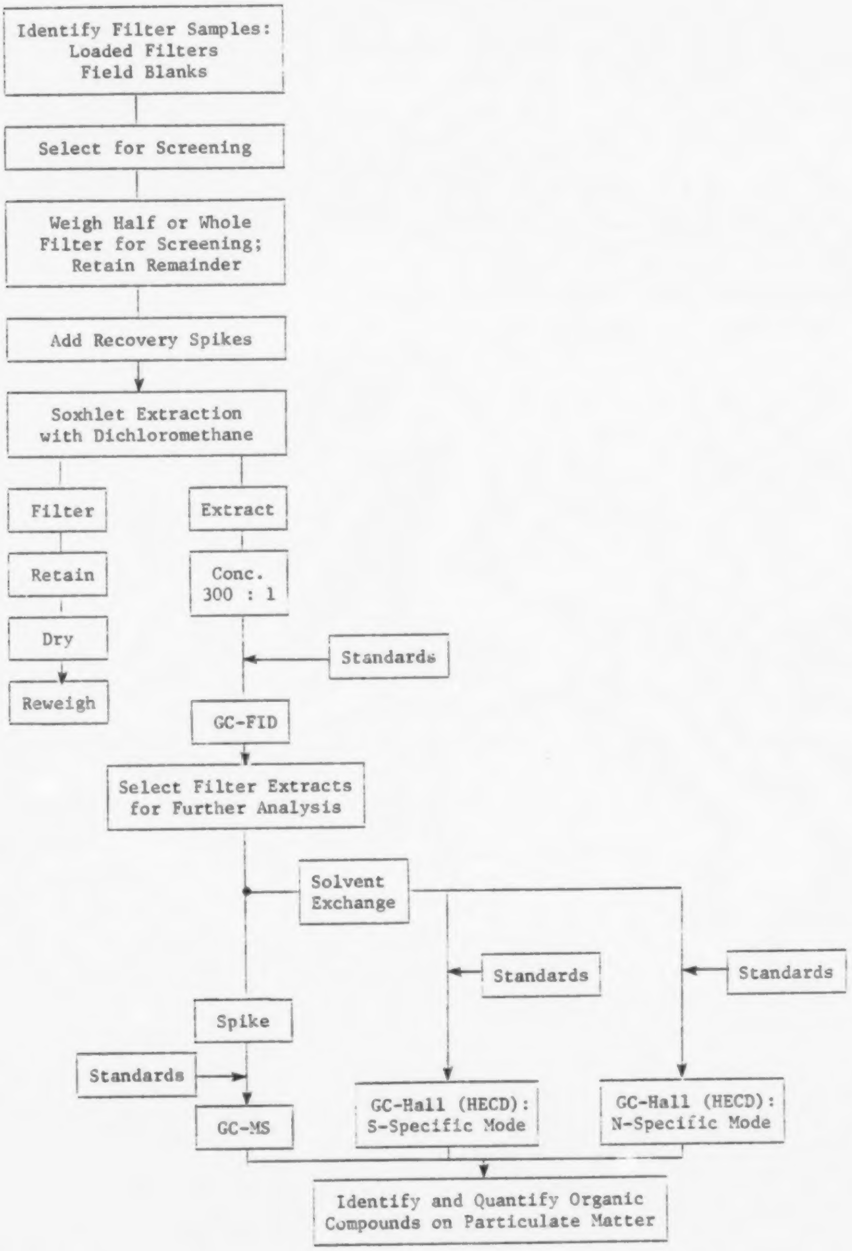

Identify Filter Samples:
Loaded Filters
Field Blanks
Select for Screening
Weigh Half or Whole
Filter for Screening;
Retain Remainder
Add Recovery Spikes
Soxhlet Extraction
with Dichloromethane
Filter
Extract
Retain
Conc.
300 : 1
Dry
Standards
Reweigh
GC-FID
Select Filter Extracts
for Further Analysis
Solvent
Exchange
Standards
Standards
Spike
Standards
GC-MS
GC-Hall (HECD):
S-Specific Mode
GC-Hall (HECD):
N-Specific Mode
Identify and Quantify Organic
Compounds on Particulate Matter

Figure 3-7. Analytical Flow Diagram for Screening and Profiling of High Volume Filter Extracts

TABLE 3-2. WORK PLAN AND MEASUREMENTS RELATED TO ANALYTICAL QA, METHODS DEVELOPMENT, AND VALIDATION

1. Verify the homogenicity of Tenax aliquots in replicate analyses.

2. Measure the Soxhlet extraction efficiency of Tenax by cyclopentane:
    a. measure recoveries of deuterated toluene and naphthalene spikes in all samples and blanks,
    b. measure recovery of five aromatics[1] spiked onto blank Tenax,
    c. analyze Tenax vapor phase samples after extraction using thermal desorption - GC-FID to determine level of unextracted sorbed species.

3. Measure the Soxhlet extraction efficiency of the HiVol filter by methylene chloride:
    a. measure recoveries of deuterated toluene and naphthalene spikes in all samples and blanks.

4. Measure the thermal desorption efficiency of Tenax:
    a. measure the short-term recovery of five aromatics[1] spiked onto Tenax immediately before analysis,
    b. measure the long-term recovery of five aromatics[1] spiked onto blank Tenax and stored for 3-4 weeks,
    c. determine the completeness of thermal desorption by subjecting one vapor sample to two successive desorption cycles.

5. Measure the extent of sample vapor breakthrough:
    a. measure the concentrations of sorbed species in pairs of front and rear (backup) Tenax traps.

6. Measure sample loss due to headspace in the sample traps and storage vials.

7. Determine appropriate packed column GC conditions for:
    a. aromatics from benzene to benzanthracene sorbed on Tenax and eluted by solvent extraction or thermal desorption,
    b. aromatics from toluene to dibenzanthracene extracted from the particulate matter caught on the HiVol filters.

8. Determine interferences in the methods by means of blank chromatograms of the extraction solvents and apparatus, and the sample collection media.

---

[1] Five aromatics = benzene, toluene, naphthalene, anthracene, benzanthracene.

TABLE 3-3. WORK PLAN FOR ANALYSES OF SELECTED KOSOVO ORGANIC SAMPLES AND GASIFICATION BY-PRODUCTS

1. Analyses of Tenax and HiVol filter samples for three sites (Sites #1, #3, and #4) sampled during the same 24-hour period (Day 5).

2. Analyses of Tenax and HiVol filter samples for the same site (Site #4 ≃ downwind) for each of the four days on which Radian's samples were collected, i.e., Days 5, 6, 7 and 8.

3. Analyses of Tenax and HiVol filter samples for one site by the different methods of separation.

4. Analyses of Tenax and HiVol filter samples for one site and comparison with the analyses of gasifier by-products (gasoline, middle oil, or tar) made under the same conditions.

Atmospheric samples from Sites #1, #3, and #4 received the first priority for screening and analysis.

Homogenization, Aliquotting, and Storage of Organic Samples

The Tenax vapor traps were prepared by Oak Ridge National Laboratory for use by the sampling crew in Kosovo. A photograph of one of the loaded traps was shown in Figure 3-3. The glass tubes are 1.2 cm ID x 15 cm and contain approximately 2.5 g of Tenax resin.

The Tenax traps were sealed after sampling at Kosovo and stored in the dark at room temperature until the start of the analytical sequence, about three months after the samples were collected.

The Tenax traps were always connected as pairs in series, one behind the other and downstream of the HiVol filter. Thus, each 24-hour sample consisted of a front and a rear Tenax cartridge and one HiVol filter. The concentrations of species sorbed on the Tenax resin was expected to be greatest near the inlet to the front trap, and to decrease in inverse proportion to the distance downstream of the inlet. Therefore, it was considered necessary to physically homogenize the Tenax resin beads from each sample trap as described below; however, resins from two traps were never mixed.

After being selected for analysis, the Tenax resin from one trap was transferred to a tared 35 mL vial which had been cleaned with chromic acid, deionized water, methanol, and methylene chloride successively, and finally fired. After sealing the vials with screw caps containing Teflon-faced septa, the vials were reweighed to determine total resin weight.

The contents of the vials were then thoroughly homogenized by hand-shaking and turning for about 5 minutes. In some cases, one-half of the homogenized resin was transferred to a second vial to produce duplicates for quality assurance studies of storage replicability.

Exposure to the ambient laboratory atmosphere was minimized by rapid transfer of resin and by resealing the vials within 10-15 seconds after opening. The resin vials were stored in a refrigerator when not in use.

HiVol filters were sealed in aluminum foil on site and were stored unopened until needed for analysis.

Extraction and Concentration of Resin and Filter Samples

A sample of 1-1.5 g of Tenax resin, precisely weighed, was transferred to a Size A (50 mL dump volume) Soxhlet extraction apparatus containing a silanized glass wool plug. The resin was spiked in the Soxhlet with 10 μL of a standard solution containing 0.94 μg/μL d_8-toluene and 1.11 μg/μL d_8-naphthalene in cyclopentane. Samples in the ∿1 g range were extracted for 24 hours with 100 mL of cyclopentane. An aliquot of 150 mL of cyclopentane was used for samples in the ∿1.5 g range. Water chilled to 10°C was constantly circulated through the Soxhlet condensor from a Brinkman constant-temperature bath.

After 24 hours, the Soxhlet apparatus was allowed to cool. The cool extract was transferred to a Kuderna-Danish flask equipped with a 10 mL graduated receiver and a 3-ball Snyder column and concentrated to a volume of 5-10 mL using a steam bath. Then the receiver was fitted with a 2-ball micro-Snyder column and the extract was further concentrated to a final volume of 0.5 mL using an oil bath.

HiVol filters were treated in a similar manner. Either the entire filter was extracted or the filter was weighed and divided in half. The half filter was reweighed and transferred to a Size E (175 mL dump volume) Soxhlet. The filter was spiked in the Soxhlet with 100 μL of the same standard used for the Tenax and extracted for 24 hours with 500 mL of methylene chloride. The extract was concentrated using the same procedure used for the Tenax extracts. The final volume of the extract varied according to extract characteristics but was always in the range of 0.5 mL to 6.0 mL. For those extracts which were analyzed with the Hall 700A electrolytic conductivity detector (HECD), a 1.0 mL aliquot of the concentrated extract in methylene chloride was solvent exchanged with cyclopentane because of interferences effects of the halogenated solvent peak on the detector. The exchange was accomplished by placing the 1.0 mL aliquot in a 10 mL graduated receiver, thoroughly mixing the aliquot with 10 mL of cyclopentane, and reconcentrating the mixture to 1.0 mL using a micro-Snyder column.

Sample Spiking

Spiking of sample and blank Tenax resins and HiVol filters was performed for the following purposes:

- to establish FID detector sensitivity, desorption efficiency and retention time parameters for thermal desorption and solvent extraction separations,
- to provide an estimation of organic loading, gross recovery and precision in blank and sample extracts by GC-FID,

- to provide reference peaks for qualitative and quantitative analyses by GC-MS, and
- to confirm tentative peak identification by peak enrichment in GC-HECD analyses.

A summary showing the sample types, standard spiking compounds, equivalent air concentrations, detection methods, and specific purposes in spiking is given in Table 3-4.

Standards were made up at ∿0.1 mg/mL in carbon disulfide or cyclopentane for thermal desorption and at ∿1.0 mg/mL in cyclopentane for solvent extraction. Spiking techniques varied according to the volume of the standard used. Standard volumes for thermal desorption were usually 1 μL and were performed with a 1μL syringe with an "in-needle" plunger to insure complete transfer of the standard from the syringe to the resin. Standard volumes for resin extract varied from ∿10- 20 μL. The spiking was performed by first pulling a small amount of cyclopentane followed by a small quantity of air into the syringe. Then the standard was pulled completely into the syringe to allow accurate quantitation with no error due to needle capacity. The cyclopentane first introduced into the syringe insured complete transfer of the standard to the resin. Filters and some storage replicability samples were spiked with larger volumes of standards from 100-700 μL. Due to the larger syringes used, the solvent plug-air bubble technique used for resins proved ineffective and no special technique was used to insure complete transfer. However, any error introduced by needle capacity was minimized by the relatively great volume of the standard in the syringe barrel.

The internal standard for extract quantitation by GC-MS was d_{10}-anthracene. The extract concentrates (0.5-6.0 mL) were spiked with a sufficient quantity of a standard consisting of 2 mg/mL d_{10}-anthracene in methylene chloride to yield a concentration of 20 ng/μL in the concentrated extracts prior to GC-MS analysis.

Quality Assurance

Resin and filter blanks were prepared to determine blank contributions to sample loadings. Blank Tenax tubes and blank HiVol filters supplied by the EPA were installed and removed from air sampling equipment on site. These blanks were handled in exactly the same manner as sample resins and filters with the exception that no air was pulled through them.

TABLE 3-4. SCHEDULE OF SAMPLE SPIKING

		Air		Purpose		
Sample or Aliquot	Spiking Compounds	Concentration Level	Detection	RT[3]	REC[4]	Ins R[5]
Tenax resin aliquot before Soxhlet extraction	d_8-Toluene d_8-Naphthalene	1.7 μg/m^3	FID & MS	X	X	X
HiVol filter aliquot before Soxhlet extraction	d_8-Toluene d_8-Naphthalene	0.07 μg/m^3	FID & MS	X	X	X
Concentrated sample extracts	d_{10}-Anthracene	----	MS	X	--	X
Blank Tenax resin aliquots before thermal desorption and before Soxhlet extraction	d_6-Benzene[1] d_8-Toluene d_8-Naphthalene d_{10}-Anthracene 1,2-Benzanthracene Benzo(a)pyrene	1.7 μg/m^3	FID & MS	X	X	X
Aerosol sample extracts	Thiophene 2-Methylthiophene 3-Methylthiophene 2,4-Dimethylthiophene 2-Ethylthiophene Benzothiophene	NQ[6]	HECD-S[7]	X	--	X
Aerosol sample extracts	3-Nitrotoluene	NQ[6]	HECD-N[7]	--	--	X

[1] By thermal desorption only.
[2] By Soxhlet extraction only.
[3] Retention time.
[4] Recovery efficiency.
[5] Instrument reponse.
[6] Not quantitatively spiked.
[7] Hall Electrolytic Conductivity Detector = HECD

The resin blanks were homogenized and aliquotted according to the procedure outlined above. Both resin and filter blanks were extracted according to the procedures outlined above and analyzed by GC-FID, GC-HECD (S- and N-specific) and GC-MS.

In addition to the analysis of sample blanks, replicate analyses were performed. For GC-FID, replicate analyses of the same extract and of different extractions of the same resin sample were performed to demonstrate extraction precision and analytical reproducibility. Replicate analyses of spiked blanks were performed by thermal desorption GC-FID to establish analytical reproducibility.

Thermal Desorption of Tenax Resin Samples

Thermal desorption of volatile organic vapors collected on polymeric sorbent resins has frequently been employed in air pollution studies. Radian's objectives in using a thermal desorption method, in addition to the Soxhlet extraction technique already described, were as follows:

- to employ a second, independent method for separating the sampled Kosovo vapors from the Tenax resin matrix,
- to use a method similar to that being applied by one of the other contract laboratories, Oak Ridge National Laboratory, to the analysis of the Kosovo Tenax samples, and
- to develop a separation method that would quantitatively desorb a wide volatility range of organics collected on Tenax, i.e., from species of C_5-C_6 (e.g., benzene) to C_{15}-C_{16} (e.g., pyrene).

Regarding the latter point, it was expected that the Soxhlet extraction methodology would cause the loss of the more volatile organics sorbed on the Tenax; e.g., benzene.

The thermal desorption assembly used by Radian consisted of three elements: 1) a thermal desorption injector shown in Figure 3-8; 2) a pre-GC column, sub-ambient vapor trap mounted in the GC oven and shown in Figure 3-9; and 3) a packed GC column. The GC effluent from the thermal desorption assembly was directed to one of two detectors during different phases of this program: to an FID in the methods development and sample screening phase and to a mass spectrometer in the emission profiling phase. In each case, $\sim$50 mL aliquots of the homogenized Tenax resin from the front or rear Kosovo vapor trap cartridges were thermally desorbed and analyzed.

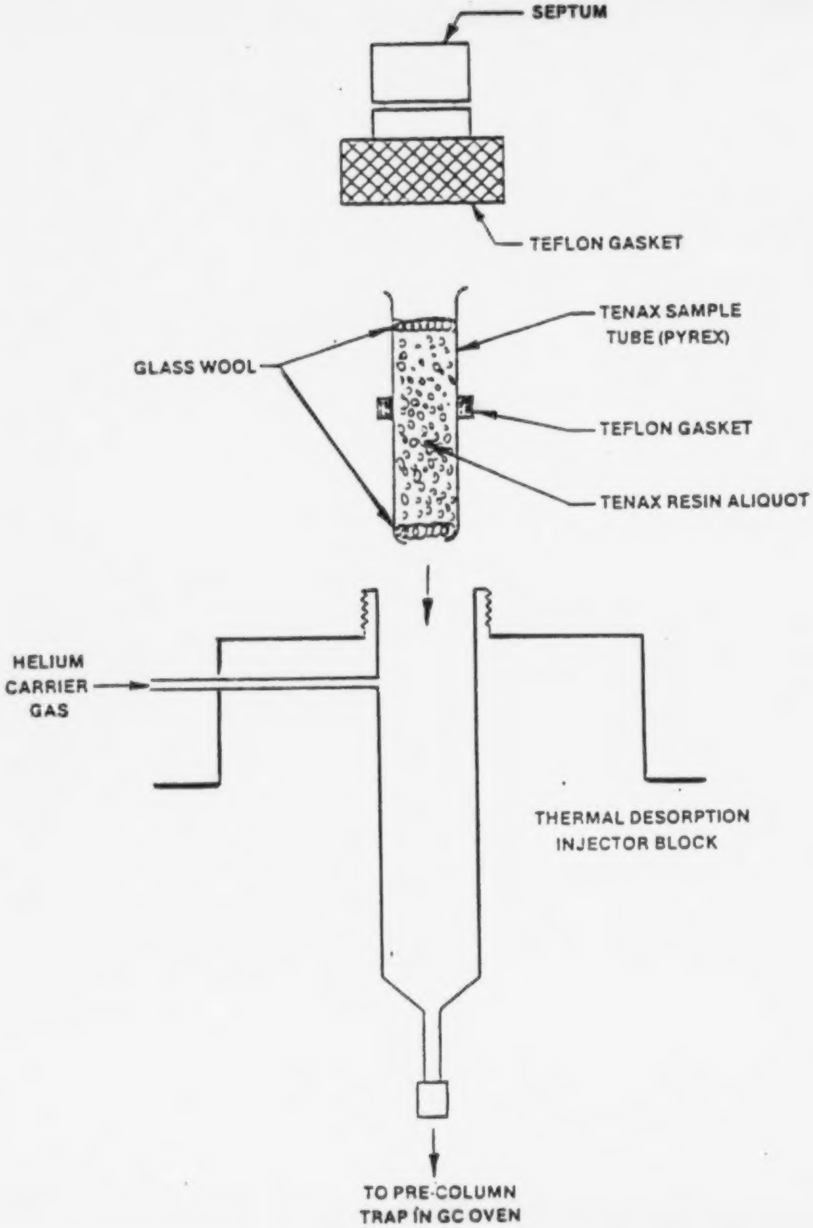

SEPTUM
TEFLON GASKET
GLASS WOOL
TENAX SAMPLE TUBE (PYREX)
TEFLON GASKET
TENAX RESIN ALIQUOT
HELIUM CARRIER GAS
THERMAL DESORPTION INJECTOR BLOCK
TO PRE-COLUMN TRAP IN GC OVEN

Figure 3-8. Schematic Diagram of the Thermal Desorption Injector Used for Tenax Resin Aliquots

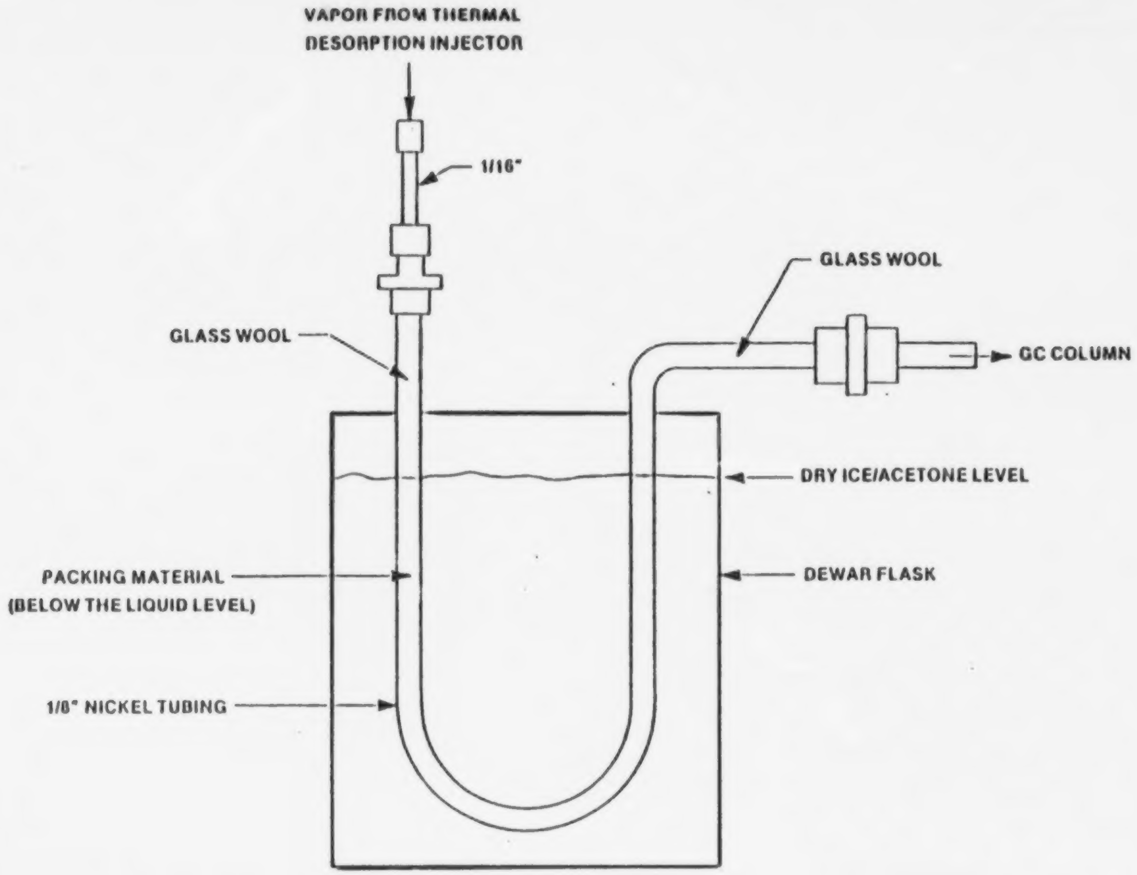

VAPOR FROM THERMAL DESORPTION INJECTOR
1/16"
GLASS WOOL
GLASS WOOL
GC COLUMN
DRY ICE/ACETONE LEVEL
PACKING MATERIAL (BELOW THE LIQUID LEVEL)
DEWAR FLASK
1/8" NICKEL TUBING

Figure 3-9. Schematic Diagram of the Sub-Ambient Pre-column Trap Assembly Used with the Thermal Desorption Injector

The thermal desorption injector shown in Figure 3-8 consisted of a modified Hewlett-Packard (H-P) injector port, which was mounted on a H-P Model 5710 GC and connected to the H-P injector block power supply and temperature control circuitry. The injector port was designed to accomodate a Pyrex glass tube, 60 mm long by 4 mm ID, which holds 0.05 g of Tenax resin between two glass wool plugs. The sample tube was fitted with a Teflon ring gasket to seal against the injector base and direct the helium carrier gas through the resin sample.

Loaded sample tubes are introduced into the thermal desorption injector by means of a threaded cap that seals with a Teflon gasket. A septum port mounted in the top of the screw cap allowed the direct injection of standard solutions into the sample tube (with and without a Tenax aliquot) without removal of the screw cap.

The thermal desorption injector was constructed of type 316 stainless steel, and the only other materials used were Teflon and Pyrex. The injector was connected by means of a short 1/16-inch stainless steel adaptor to the nickel pre-column trap and the nickel packed GC column. The desorbed sample vapors thus were in contact with glass, stainless steel (for a pathlength of ∿2 cm) and nickel.

The pre-column trap (see Figure 3-9) consisted of a 12 in section of 1/8" OD nickel tubing packed with the same material as the GC column: 10% OV-101 on 80/100 mesh Supelcoport. The trap was immersed in a dry ice and acetone bath when the Tenax sample was being desorbed and was at the (programmed) GC oven temperature the rest of the time. The GC column used was 3 m (10 ft) by 2mm ID nickel, packed with 10% OV-101 on 80/100 mesh Supelcoport and temperature programmed between 50 and 250°C at 16°C/min after a 4 minute hold. A helium carrier gas flow rate of 30 mL/min was used.

The timed sample introduction sequence was as follows:

1. An empty glass sample tube with both glass wool plugs in place was cleaned by placing it in the hot (250°C) thermal desorption injector for at least 10 minutes under a helium carrier flow.

2. The cleaned sample tube was removed from the injector and allowed to cool. The GC oven was cooled, the oven door opened and the oven fan was turned off.

3. A dry ice/acetone bath in a Dewar flask was placed around the pre-column trap at least two mintues before the Tenax sample was loaded in its glass tube.

4. A Tenax sample aliquot was loaded into the cleaned sample tube by removing the upper glass wool plug and carefully pouring the resin from its storage vial directly into the sample tube. The sealed vial containing the homogenized Tenax remained open only the 10-20 sec necessary to transfer the sample. The tared vial (plus Tenax) was weighed after the transfer to measure the size of the aliquot. The weight of a typical aliquot was approximately 50 mg which represented approximately 2% of the 2.5 g of Tenax initially held in each Tenax vapor trap cartridge.

5. Immediately after transferring the Tenax aliquot, the storage vial was closed, the upper glass wool plug replaced, the Tenax sample was spiked with deuterated internal standard aromatics (as desired), the thermal injector cap was removed, the sample tube was pushed down to the bottom of the thermal desorption injector well, and the cap was replaced.

6. It was determined, after experimentation, that a single 10 minute thermal desorption cycle with the injector at 250°C and a helium carrier gas flow of 30 mL/min was sufficient to desorb organics through pyrene/benzoanthracene (MW = 202). The desorbed vapors were collected in the pre-column trap held at the dry ice/acetone temperature (-77°C).

7. At the end of the 10 minute desorption period, the dry ice/acetone bath was removed, the oven door was closed, and the GC column temperature program was initiated: 50°C isothermal for 4 minutes, 16°C/minute to 250°C and 250°C isothermal for a total GC analysis time of approximately 30 minutes or until the GC trace regained its initial baseline level. The helium flow rate was maintained at 30 mL/min. The FID detector or the GC-MS transfer line were held at a temperature of 250°C.

8. The total cycle time for tube cleaning and loading, thermal desorption and GC-FID (or GC-MS) analysis, followed by oven cooling was about one hour.

The standard compounds shown in Table 3-4, dissolved in either carbon disulfide or cyclopentane, were used to establish retention time, determine thermal desorption efficiencies and, as internal spikes, to determine semi-quantitative amounts of the desorbed organics. Desorption efficiencies were obtained by comparison of the peaks obtained when the standard compounds were injected directly into an empty glass sample tube to those obtained when the standards were carefully spiked onto the Tenax and then desorbed. However, the dry ice/acetone trap and the same 10 minute desorb cycle were still used for direct injection.

The spiking of standard compounds onto Tenax was carried out with resin which had previously been desorbed to remove any impurities. Extreme care was taken to spike the standard solution onto the Tenax itself and not onto the glass tube. The spiked blank Tenax was immediately desorbed onto the cold pre-column in the same manner as the Tenax samples and the directly injected standards.

3.4.3 Sample Screening by GC-FID

Instrumentation

Two different gas chromatographs were used for sample screening by GC-FID: a Tracor Model 560 for Soxhlet extracts of the HiVol filters and the Tenax, and a Hewlett-Packard Model 5710 for the thermal desorption of the Tenax samples. In both cases, chromatograms were usually recorded and peaks integrated with a H-P Model 3380A electronic integrator.

Equivalent GC columns were used with each instrument for the GC-FID screening: 3 m (10 ft) x 2 mm ID columns packed with 10% OV-101 on 80/100 mesh Supelcoport, although the Tracor column was Pyrex and the H-P was nickel. Small differences also existed in the operating conditions.

	Hewlett-Packard 5710 GC-FID	Tracor 560 GC-FID
Carrier	He, 30 mL/min	N_2, 30 mL/min
Injector	250°C	250°C
Detector	250°C	300°C
Temperature Program	50°C for 4 minutes 16°C/min to 250°C, hold	50°C for 5 minutes 20°C/min to 250°C, hold

Standard Compounds for Qualitative and Quantitative Analysis

The following standard compounds were injected to establish retention time parameters:

Normal Hydrocarbons:	C_7 through C_{17} and C_{20}
Aromatic Hydrocarbons:	Benzene Toluene o-Xylene m-Xylene p-Xylene

Polynuclear Aromatics:	Naphthalene Anthracene 1,2-Benzanthracene 1,2,5,6-Dibenzanthracene Benzo(a)pyrene
Nitrogen and Sulfur Species:	Aniline Thiophene

The quantitative standard used contained d_8-toluene at 0.94 mg/mL and d_8-naphthalene at 1.11 mg/mL in cyclopentane, as shown in Table 3-4.

Objectives of Sample Screening by GC-FID

All resin and filter extracts were routinely screened by GC-FID prior to other analyses. The objectives of sample screening were:

- to provide an estimation of sample loading and complexity,
- to provide a gross estimation of extraction efficiency by comparing the recovery of deuterated toluene and naphthalene to standard chromatograms of toluene and naphthalene,
- to provide an initial sample characterization by comparing sample chromatograms to chromatograms of standard compounds,
- to aid in the selection of samples for further analysis based on the preceding criteria, and
- to act as an aid to analysis by GC-MS and HECD.

3.4.4 Chemical Speciation Methods for Gasification Plant Emissions

The GC-FID screening chromatograms of the ambient air samples and gasifier by-products indicated the presence of a complex mixture of more than 50 organic compounds. In order to validate the analytical methods being used and to identify organic compounds in the ambient air samples, it was necessary to perform additional analyses to obtain a chemical speciation.

In the work described here, three methods of identification were used:

- GC-Mass Spectrometry (GC-MS),
- GC-Hall Electrolytic Conductivity Detector in the sulfur-specific mode (GC-HECD/S), and
- GC-Hall Electrolytic Conductivity Detector in the nitrogen-specific mode (GC/HECD/N).

This combination of detectors was selected to achieve the following results:

- tentative identification of all the major and most of the minor organic pollutants, and
- development of a profile of the emissions with regard to sulfur- and nitrogen-containing compounds against the much higher hydrocarbon emission profile.

A description of each method used for chemical speciation follows.

HECD - Sulfur Mode

The Hall Electrolytic Conductivity Detector can be operated in a sulfur-specific oxidative mode by combining the chromatographic effluent with air in a microreactor. The gaseous reaction products, carbon (CO/CO_2), halogen (HX), nitrogen (NO_2), sulfur (SO_2), and oxygen (H_2O), are directed to a differential conductivity cell. The HX is removed by the S-mode scrubber and the cell response to H_2O, CO_x, and NO_x is much less than that to SO_2. The HECD can achieve a discrimination ratio of sulfur/hydrocarbons of approximately 10^6 and a linear response range of 10^4. The sensitivity of the HECD in sulfur-mode is of the same order of magnitude as the FID for hydrocarbons, i.e., approximately 5×10^{-12} g/second.

Ambient air sample extracts and gasifier by-product solutions were injected into a Tracor 560 GC with a Tracor 700A HECD. The output chromatogram yielded a profile of the sulfur-containing compounds in the sample, i.e., the number and levels of the sulfur species. This constitutes a speciation of the sample and is an aid in the specific compound identifications by MS. Selected compound identifications were established by injecting authentic standards and comparing retention times.

HECD - Nitrogen Mode

When the Hall Electrolytic Conductivity Detector is operated in a nitrogen-specific reductive mode, the components eluting from the GC column are combined with hydrogen to form gaseous reaction products as follows:

carbon:	CH_4
halogen:	HX
nitrogen:	NH_3
sulfur:	H_2S
oxygen:	H_2O

The HX and H_2S are removed in a N-mode scrubber and the conductivity cell has no response to the CH_4 and H_2O. The HECD can achieve a nitrogen-specific response ratio of nitrogen/hydrocarbons of $\geq 10^6$, with a linear response range of 10^4. The HECD sensitivity in N-mode is comparable to its sensitivity in S-mode and to that of a FID for hydrocarbons.

The speciation produced by the HECD in N-mode is exactly analgous to that given in the S-mode, i.e., the number and levels of the N-containing compounds in the sample.

HECD Instrumentation and Methods

A Hall Model 700A Electrolytic Conductivity Detector was mounted on a Tracor 560 gas chromatograph. The detector was used in both the nitrogen and sulfur selective modes. A Hewlett-Packard Model 3380A integrator was used to integrate peak areas.

The following conditions were used in the selective modes:

Sulfur Mode

Carrier Flow:	He, 35 mL/min
Injector Temperature:	250°C
Detector Base Temperature:	225°C
Reactor Temperature:	850°C
Oven Temperature:	50°C for 5 minutes, 20°C/minute to 250°C hold at 250°C
Column:	10 percent OV-101 on 80/100 mesh Supelcoport, 3 m (10') x 2 mm ID glass

Nitrogen Mode

Carrier Flow:	He, 35 mL/min
Injector Temperature:	250°C
Detector Base Temperature:	225°C
Reactor Temperature:	850°C
Oven Temperature:	50°C for 5 minutes, 20°C/minute to 250°C hold at 250°C
Column:	10 percent Apiezon L, 2 percent KOH on 80/100 Chromosorb W AW, 3 m (10') x 2 mm ID glass column

Extractions of the Tenax and HiVol air samples were performed as described. However, due to the incompatability of methylene chloride (used for HiVol extraction) with the HECD, a solvent exchange to cyclopentane was made.

The concentrated extracts of the air samples and the gasifier by-products were introduced into the gas chromatgraph by injection of the liquid. The air sample extracts were injected in the 1 to 10 microlitre range while the undiluted by-products were injected at the tenths of a microlitre level.

An additional extraction was performed in connection with the sample characterization by the HECD-N detector. The gasification by-product, medium oil, was extracted with an aqueous acid solution to separate the basic compounds. The aqueous extract was neutralized and back extracted with cyclopentane to place the organic compounds in an organic solvent. This fraction was termed the basic extract of medium oil and it was analyzed by HECD-N and GC-MS. The removal of non-basic N-containing compounds and the reduction of the hydrocarbon concentrations aided in the speciation of the N-compounds in the middle oil and in the atmospheric samples.

Mass Spectrometry

Selected air samples and gasifier by-products were analyzed by GC-MS and the mass spectra data were interpreted to yield molecular identities. This was performed for analytes produced both by the thermal desorption and solvent extraction of the ambient air samples, as well as for extracts and solutions of some of the gasifier by-products.

The purpose of chemical speciation by mass spectrometry was to yield a tentative molecular identification of the major organic species in the samples analyzed and to search for potentially harmful minor and trace components whose presence might be inferred on the basis of the major components.

To achieve these ends, a Hewlett-Packard GC-MS system (a Model 5985 or Model 5980) was operated in a electron-impact, mass-scanning mode, with GC-MS data recorded on disc memory. The operation parameters were as follows:

Ionization electron energy:	70 eV
Scanning mass range:	40 - 320 amu
Mass scan speed:	∿3 sec/280 amu
Retention time range:	2 - 60 minutes

Mass spectrometric identifications were made by manual examination of three different displays of the recorded GC-MS data:

- Total Ion Current (TIC) Chromatogram: a trace of the sum of all ion current regardless of mass versus GC retention time,
- Selected Ion Current Chromatogram: a trace of the ion current due to one selected mass number versus GC retention time, and
- the mass spectrum, with any background subtracted.

An individual component identification (or tentative identification) was made based on consideration of each of the following data elements:

- the absolute retention time of standard compounds and the relative retention times of other tentatively identified compounds, including homologs;
- the comparison of the mass spectrum with standard reference spectra generated by Radian (e.g., for the Priority Pollutant PNA's) or tabulated in the literature (e.g., the 8 Peak Index of Mass Spectra);
- a search for the three most intense ions in the mass spectrum of a suspected compound, always including the molecular ion M^+, and for their simultaneous peaking at a single, reasonable retention time;
- the GC-FID screening chromatogram and the profiles generated by HECD/S- and /N-specific detection; and,
- the simultaneous occurrence of the same tentatively identified compound in different aliquots of ambient aerosol samples and in the gasifer by-products.

3.4.5 Quantitation of Pollutant Concentrations

Two levels of pollutant quantitation were carried out in this work:

- an accurate quantitation of a relatively few pollutant concentrations based on the use of standard compounds for the measurement of recovery and sensitivity factors, e.g., separation recovery % or individual GC-FID or GC-MS instrumental response factors, and
- a semi-quantitation (accurate to within ± 2X) for the majority of the reported pollutants, based on the assumption of constant or unity recovery and sensitivity factors for whole groups of compounds, e.g., assuming the same GC-MS sensitvity for all alkyl benzenes as for benzene.

Each method of quantitation is discussed below in its appropriate detector section.

Quantitation of Toluene and Naphthalene by GC-FID

Since the FID detector cannot distinguish non-deuterated compounds from their deuterated homologs and since all samples were spiked with d_8-toluene and d_8-naphthalene prior to extraction and GC-FID analyses, quantitation of toluene and naphthalene by GC-FID was limited to the gross yield of these compounds contributed by both the sample and the spikes.

Quantitation was accomplished by comparing the peak areas of toluene and naphthalene in the sample extracts to the peak areas of standard compounds at known concentrations. Concentrations were estimated using the following equation:

$$C_1 = \frac{A_1}{A_2} \times \frac{m_2}{v}$$

where: C_1 = the concentration of the compound present in the sample extract in ng/μL,

A_1 = the area count of the peak in the sample extract,

A_2 = the area count of the peak in the standard,

v = the volume of the sample extract injected, in μL, and

m_2 = the mass of the standard compound in ng.

Although direct quantitation of sample contribution was not possible, sample contribution could be determined by calculating the proportion of non-deuterated toluene or naphthalene from mass spectra data and multiplying the gross quantity from GC-FID by this factor.

Quantitation of Sulfur- and Nitrogen-Containing Species by GC-HECD

Nitrogen- and sulfur-containing species were quantitated by comparing peak areas in sample chromatograms to peak areas of 3-nitrotoluene and thiophene, respectively. For both 3-nitrotoluene and thiophene a response curve was generated by injecting standard solutions over a range of concentrations and plotting integrated areas versus the mass (in ng) of compound. Sample peaks were quantitated by comparing their areas to the response cuve. The reported atmospheric concentrations for S- and N-containing species are expressed in units of μg thiophene (C_4H_4S)/m^3 and μg nitrotoluene ($C_7H_7NO_2$)/m^3, respectively.

Toluene and Naphthalene Quantitation by GC-MS

The calculation of an accurate concentration level by GC-MS is based on the equation:

$$C_{n,air} = C_{a,extr.} \left(\frac{An}{Aa}\right)\left(\frac{1}{RRF}\right) \times \frac{V_{extr.}}{V_{air}} \times \frac{1}{Aliq.} \times \frac{1}{REC}$$

where: C_n, air = concentration of the pollutant N in the ambient aerosol in μg/m^3.

C_a, extr. = concentration of the internal standard A in the sample extract in μg/μL.

An/Aa = ratio of peak areas of pollutant N to internal standard A, usually both measured for the molecular ions.

RRF = relative response factor defined by a separate measurement of peak areas for equal concentrations of A and N, i.e., Aa = An/RRF when $C_a = C_n$

V extr. = final volume of sample extract, in μL.
V air = volume of air originally sampled in m^3.

Aliq = fraction of original air sample represented by extract aliquot.

REC = fractional overall recovery of pollutant N in the collection, separation and concentration processes, i.e. , $REC = (REC)_{samp.} \times (REC)_{sepr.} \times (REC)_{conc.}$

The quantities RRF and REC are compound specific and must be measured for each component N to achieve an accurante quantitation.

Semi-quantitation is based on the approximations:

RRF = 1 and
REC = 1 or a constant

for any other pollutant P. When the internal standard A and the pollutant P are chemically similar, the semi-quantitation based on the above approximation is accurate to within a factor of two.

SECTION 4

RESULTS AND DISCUSSIONS

The total set of Kosovo ambient aerosol samples, 16 days x 5 sites, were distributed among cooperating laboratories in the U.S. and Yugoslavia according to the schedule presented in previous sections. At Radian, aerosol samples were prioritized for analysis by the methods described in Section 3. The results of these analyses, including the meteorological monitoring during sampling, are discussed below under four headings:

- the meterological data,
- the QA results for the sampling procedures.
- the physical and inorganic characterization of the particulate matter, and
- the trace analysis and QA measurements of the organic components in the Kosovo aerosol, both on the particulate matter and in the vapor phase.

The LoVol filters were weighed at the Kosovo Institute. In addition to the gravimetric analysis, both Radian and the Yugoslavs (at INEP in Belgrade) were to perform the following analyses:

- extraction (chemical and/or thermal) of the Tenax organic vapor trap resins and HiVol filters followed by GC and GC-MS analysis for organic speciation;
- inorganic ion chromatographic analysis of LoVol filters for $SO_4^=$, Cl^-, NO_3^-, NH_4^+, and Na^+;
- C, H, N, S elemental analysis;
- carbon speciation; and,
- multi-element analysis (PIXE).

In addition, Radian performed multi-element analysis (ICAP) of the LoVol filters and scanning electron microscopy (SEM) of selected filters. Radian also analyzed the reduced meteorological data supplied by the EPA.

4.1 METEOROLOGICAL RESULTS

Meteorological monitoring throughout the sampling period was an integral part of this ambient sampling program. A Climatronics meteorological station (located at Site #5) recorded time, temperature, solar flux, wind speed and direction, and atmospheric pressure. These data were recorded on magnetic tape (Datel Data Logger II) and a copy of the results, including 2-, 6-, and 24-hour averages, were provided to Radian by the EPA personnel who processed the data.

Of interest to the atmospheric sampling effort is the percentage of time that each station was located downwind from the plant. The wind direction indicator on the Climatronics unit was resolved into only eight quadrants, representing 45-degree corridors. Since there were no details of the horizontal plume dispersion within a 45° corridor, the contribution of wind direction to the percent (of time) downwind for a site was decreased in direct proportion to the wind direction angle away from that site. That is, if the wind was blowing directly at the site, the contribution would be 1.00 times the duration of wind in that direction. If the wind was blowing at 45° or more from the site, the contribution was zero; if 22.5°, the contribution was 0.50.

For example, Site #1 was 15° east of due north or 30° north of northeast (see Figure 2-2). The contribution at this site was taken to be two-thirds of a south wind and one-third of a southwest wind. This weighted average was done for each wind class (each 5 km/hr) given in the data. Table 4-1 gives the distribution of the sampling sites and the weighted wind directions used to calculate the percentage downwind. The 6-hour and the 24-hour averages were taken from the data supplied by EPA. The results are given in Table 4-2 as percent of time that the sampling site was "downwind" from the gasifier facility, and as the weighted average wind speed in that direction.

The percentage of time that a site was downwind was correlated with the data taken from the HiVol and LoVol filters and the Tenax resin. A site that was at all times upwind can serve as a background reading. Also included in Table 4-2 are qualitative notes recorded at the time by the site sampling personnel. They reflect general weather data and plume behavior, when distinctive, and are intended to complement the meteorological data. Figure 4-1 presents a textbook representation of various plume categories. The behavior of the plume reflects the stability (lapse rate) of the local atmosphere.

TABLE 4-1. PARAMETERS USED TO CALCULATE PERCENT DOWNWIND FOR EACH SITE

Site #	Compass Heading From Gasifier	Approximate Distance (km)	Directional Vector
1	15°	2.0	0.67S + 0.33SW
2	90°	1.0	1.00W
3	150°	1.7	0.67NW + 0.33N
4	215°	1.0	0.22N + 0.78NE
5	315°	2.2	1.00SE

TABLE 4-2. METEOROLOGICAL DATA FOR THE AMBIENT AIR SAMPLING PROGRAM

	Location Compass Wind Mix		Site #1 15° .67 S + .33 SW		Site #2 90° W		Site #3 215° .67 NW + .33 N		Site #4 215° .78 NE + .22 N		Site #5 315° SE	
DAILY NOTES	Day/ Time	Temp. C°	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr
18 May 1979 - Early morning inversion, fanning plume; no clouds. Gasifier odor at 3 and 4. Clouds build to afternoon rain.	138/	14.2	0.6	2.5	5.7	2.9	18.7	5.6	40.0	7.6	1.1	3.9
	0-6	7.1	0	---	10.0	2.5	7.0	2.5	61.0	2.6	1.0	2.5
	6-12	16.8	0	---	7.0	2.9	39.0	5.0	20.0	7.0	0.0	---
	12-18	20.1	0	---	0.0	---	12.0	12.8	59.0	12.0	1.0	5.0
	18-24	12.8	1.0	2.5	8.0	3.3	20.0	5.5	31.0	5.1	2.0	3.7
19 May 1979 - Early morning inversion, fanning plume. Looping plume (8-9 AM). Plume touchdown @ 4 AM at fence line. Clouds building in afternoon.	139/	15.9	1.0	2.5	3.6	3.6	14.8	5.5	45.2	8.6	1.1	2.5
	0-6	8.0	1.0	2.5	3.0	2.5	13.0	2.5	41.0	2.6	3.0	2.5
	6-12	17.3	1.0	2.5	7.0	4.3	26.0	5.1	31.0	7.0	1.0	2.5
	12-18	23.0	0.0	---	0.0	---	13.0	13.5	60.0	14.2	0.0	---
	18-24	15.2	2.0	2.5	5.0	3.1	14.0	4.9	45.0	6.7	1.0	2.5
20 May 1979 - Same pattern as previous day; no rain.	140/	17.0	0.7	2.5	3.0	2.5	15.7	5.0	39.4	7.1	1.3	2.5
	0-6	9.7	0.0	---	9.0	2.5	16.0	2.5	42.0	3.3	2.0	2.5
	6-12	19.4	0.0	---	1.0	2.5	31.0	5.5	32.0	8.8	1.0	2.5
	12-18	23.7	0.0	---	0.0	---	4.0	13.5	47.0	10.8	0.0	---
	18-24	15.2	2.0	2.5	5.0	2.5	5.0	2.5	40.0	3.1	4.0	2.5
21 May 1979 - Morning inversion; plume over Obilić. Sunny, cumulus build-up. Afternoon thunderstorms in area.	141/	17.6	10.4	4.3	14.8	6.3	16.1	5.4	18.4	3.5	6.1	2.8
	0-6	10.9	9.0	2.5	9.0	2.5	10.0	2.6	26.0	2.5	10.0	2.5
	6-12	20.3	7.0	4.1	17.0	3.4	17.0	2.8	18.0	3.0	4.0	2.5
	12-18	23.7	12.0	6.0	27.0	9.2	17.0	7.2	9.0	5.6	4.0	3.9
	18-24	15.4	12.0	3.6	4.0	3.2	20.0	6.7	23.0	3.7	7.0	2.5

TABLE 4-2. (Continued)

DAILY NOTES	Location Compass Wind Mix		Site #1 15° .67 S + .33 SW		Site #2 90° W		Site #3 215° .67 NW + .33 N		Site #4 215° .78 NE + .22 N		Site #5 315° SE	
	Day/ Time	Temp. C°	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr	% DNWD	Vel km/hr
22 May 1979 - Partly cloudy, warm. Fanning plume (8-9), lofting plume (10-12), coning plume (midafternoon), fanning plume (17-19 hours).	142 /	16.9	2.0	2.5	1.4	2.5	16.0	6.2	46.5	9.4	0.3	2.5
	0-6	11.2	10.0	2.5	6.0	2.5	9.0	3.4	34.0	3.1	2.0	2.5
	6-12	18.4	0.0	---	1.0	2.5	20.0	7.6	48.0	11.3	0.0	---
	12-18	22.1	0.0	---	0.0	---	18.0	8.8	48.0	10.8	0.0	---
	18-24	15.7	0.0	---	0.0	---	16.0	5.5	50.0	7.1	6.0	7.5
23 May 1979 - Cloudy; variable local winds. Early morning fanning —> lofting —> coning. Heavy afternoon thunderstorm.	143/	15.7	7.5	7.4	2.9	3.3	14.0	4.6	29.2	5.1	10.0	6.2
	0-6	10.9	0.0	---	1.0	2.5	16.0	3.8	49.0	4.9	0.0	---
	6-12	18.1	0.0	---	0.0	---	25.0	5.7	34.0	6.7	2.0	7.5
	12-18	20.4	24.0	7.9	7.0	3.8	2.0	4.4	3.0	7.1	31.0	6.5
	18-24	13.2	4.0	2.5	5.0	2.5	13.0	3.3	32.0	3.0	5.0	2.5
24 May 1979 - Morning calm. Scattered clouds, warm. Local winds. Lofting plume (morning) —> coning; good vertical mixing. Late afternoon thunderstorm.	144 /	14.6	17.2	4.6	8.0	3.2	11.0	5.1	14.7	3.8	13.0	4.3
	0-6	9.7	10.0	2.5	5.0	2.5	9.0	2.5	31.0	2.5	13.0	2.5
	6-12	17.2	30.0	3.9	11.0	2.8	4.0	2.8	3.0	2.5	20.0	3.9
	12-18	18.9	35.0	9.1	11.0	4.0	15.0	8.4	16.0	6.3	8.0	8.2
	18-24	12.5	15.0	2.9	3.0	2.5	15.0	3.1	15.0	3.1	11.0	3.7
25 May 1979 - Morning fog. Fanning —> lofting —> coning plume; touchdown in obilic. Sunny, medium/high scattered clouds. Good vertical mixing.	145/	16.4	24.8	4.7	15.2	4.2	4.3	3.2	11.2	4.7	6.5	4.5
	0-6	10.2	34.0	2.8	8.0	2.5	9.0	2.5	11.0	2.5	2.0	2.5
	6-12	15.8	37.0	2.6	14.0	2.7	2.0	2.5	0.0	---	11.0	4.3
	12-18	23.8	22.0	5.9	25.0	5.9	2.0	5.7	5.0	8.5	8.0	5.2
	18-24	15.7	5.0	3.4	10.0	2.8	6.0	3.5	20.0	4.7	3.0	3.8

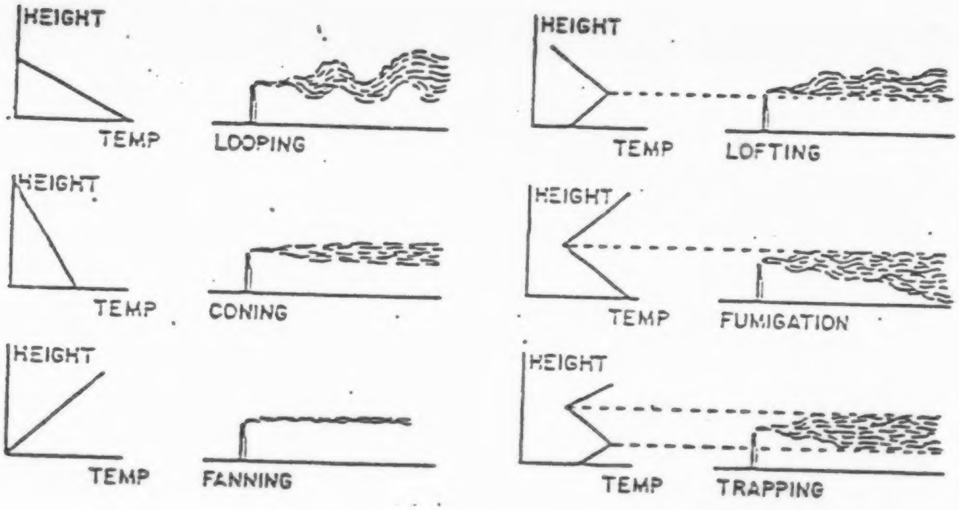

HEIGHT
TEMP
LOOPING
HEIGHT
TEMP
LOFTING
HEIGHT
TEMP
CONING
HEIGHT
TEMP
FUMIGATION
HEIGHT
TEMP
FANNING
HEIGHT
TEMP
TRAPPING

Figure 4-1. Pictorial Definition of Plume Types

4.2 QUALITY ASSURANCE RESULTS FOR SAMPLING PROCEDURES

Quality assurance activities for sampling included sampling supervision, duplicate weighings, completeness of logs, and flow audits. These served to verify that conditions were normal or unchanged. If there was a discrepancy noted, corrective action was taken at that time.

The LoVol filters were equilibrated and weighed before and after sample collection in the Kosovo Institute Laboratory using a Model 30/36 Microbalance loaned to EPA for this study by the Mettler Instrument Company. To evaluate the effect of systematic errors due to instrument drift or change in atmospheric conditions, reference objects (a brass ferrule and two blank filters) were weighed daily and the results plotted against humidity, temperature and pressure. Table 4-3 presents a summary of the information contained on these graphs. Slight trends were indicated for LoVol filter paper (#1 and #2) vs. temperature (0.04 mg/°C, negative) and for LoVol filter paper (#2) vs. humidity (0.04 mg/%, positive). These trends were not identified or established sufficiently well to warrant correction of the data. The most pronounced trend was for filter paper vs. date, indicating some persistent change with time. However, while one piece of filter paper lost weight, the other gained. Thus, these measurements are most useful only as an indication of the magnitude of the scatter. The operator technique appeared satisfactory since the weight of the metal object had no trend, and the scatter was an order of magnitude smaller than the scatter for the filters.

At random times during the project, filters likewise chosen at random were reweighed in the Kosovo labs by Radian scientists. Differences averaged about ± 0.022 mg for 34 weighings and were random. The daily reweighing of 10 percent of the filters confirmed that the weighings were repeatable. Several gross discrepancies were noted and the procedure was corrected at the time. At the end of the sampling effort, it was discovered that the balance operator during the final four days of testing incorrectly recorded the weights. The Yugoslavian scientific team who ultimately received the data covering this period have been so advised.

4.3 PHYSICAL AND INORGANIC RESULTS

4.3.1 Particulate Loading

One phase of the sampling effort was the simultaneous collection of the total and the <2 μm aerosols. The mass of these catches was determined gravimetrically to quantitate the atmospheric aerosol mass loading. These data are given in the data volume associated with this report.

In order to determine the contribution from the gasifier complex, the mass loadings were plotted against the percentage of time that the collection site was downwind from the gasifier. Sites that were zero percent downwind were considered representative of the ambient conditions, unaffected by the gasifier.

TABLE 4-3. SUMMARY OF RESULTS ON WEIGHING CONTROLS (All Weights in mg)

Object	Variables (range)	Arithmatic* Mean Weight	High Weight	Low Weight	± σ
Metal Ferrule	Pressure (738.5-743.5 mmHg) Temperature (19.0-25.0°C) Humidity (51.8-58.0)	243.978[1]	243.997	243.965	0.007
LoVol Filter Paper (#1)	Pressure (738.5-743.5 mmHg) Temperature (19.0-25.0°C) Humidity (51.8-58.0)	151.860[2]	152.008	151.633	0.08
LoVol Filter Paper (#2)	Pressure (738.5-743.5 mmHg) Temperature (19.0-25.0°C) Humidity (51.8-58.0)	150.900[3]	150.987	150.782	0.06

*Range in which 68% of values were found.
[1]- 101 weights.
[2]- 49 weights.
[3]- 44 weights.

A comparison of upwind and downwind sampling sites reflects the impact of the complex on air quality. Figure 4-2 is a plot of <15 µm and <2.0 µm aerosols versus percent downwind. The approximate ambient aerosol particulate loading was about 100 $\mu g/m^3$ with about 25 percent in the fine particle range (<2 µm). Downwind of the Kosovo complex, the loadings increased significantly.

A regression analysis for both <15 µm and <2 µm particles produced the least squares linear plots represented on Figure 4-2. The correlation coefficient for both lines is 0.62; 41 and 44 points were used to determine these lines, and statistically there is a greater than 99.9 percent certainty that a trend does exist. The actual equations are:

<15 µm particles, $y = 3.683x + 85.8$
(correlation = 0.62, 41 points)

< 2 µm particles, $y = 0.749x + 23.7$
(correlation = 0.62, 44 points)

These data show a marked increase in total particles as the percent downwind parameter increases. The intercepts should represent the atmospheric concentrations upwind of the plant; i.e., they should represent the ambient air background levels.

The ambient ratio of the total-to-fine particles was 85.8/23.7 = 3.62, but the ratio of the rate of increases (the slopes) was 3.68/0.75 = 4.91. This suggests that the additional particulate matter collected downwind from the Kosovo Industrial Complex has a somewhat higher ratio of large particles-to-fines than does the ambient particulate matter.

4.3.2 Chemical Loadings

The data for total sulfur and sulfate, when plotted as concentration against percent downwind, showed no trend (see Figures 4-3 and 4-4). The least squares straight line is nearly flat (indicating no variation), and the correlation coefficients are very low (indicating substantial uncertainty for the presence of a trend). For total sulfur:

<15 µm particles, $y = 0.07x + 3.98$
(correlation = 0.42, 17 points)

< 2 µm particles, $y = 0.02x + 3.00$
(correlation = 0.16, 17 points)

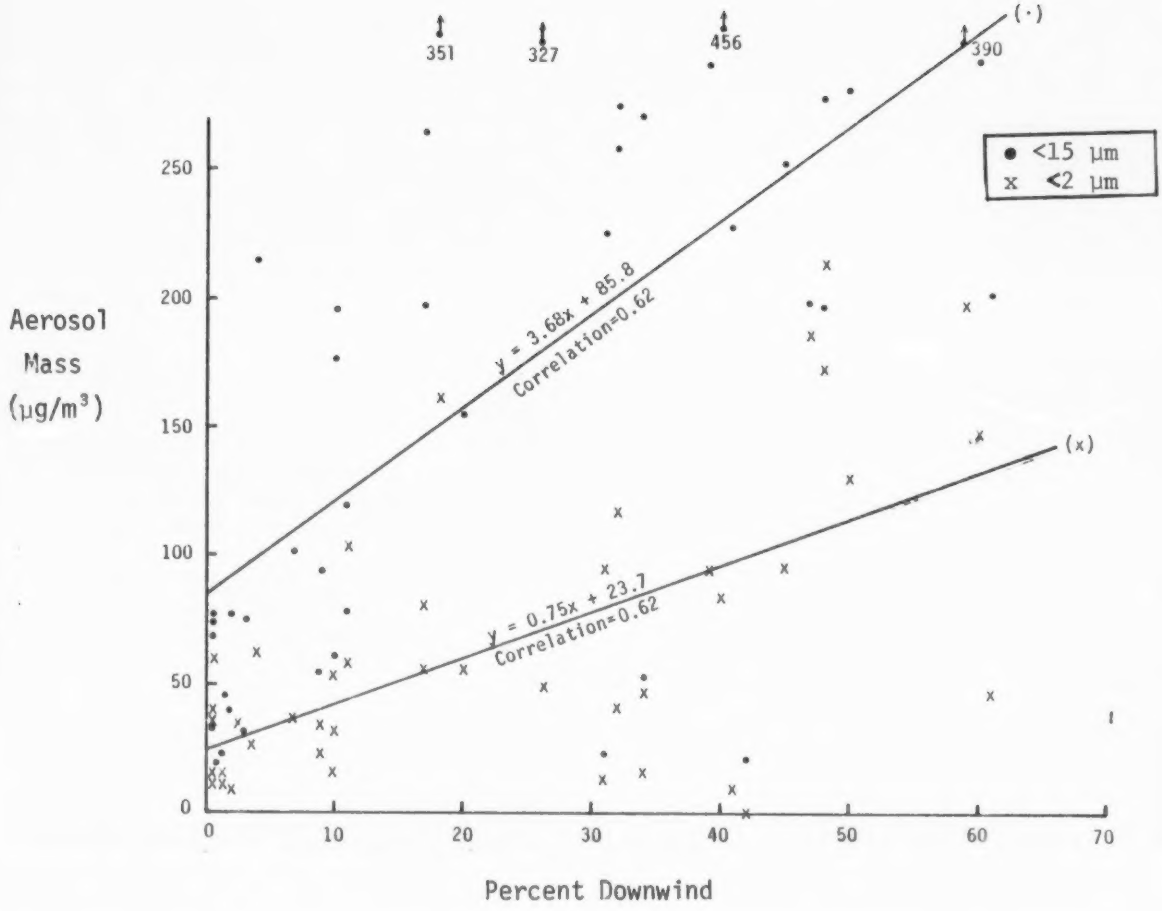


Figure 4-2. A Plot of the <15 µm and <2.0 µm Particle Fractions versus Percent Downwind. The Lines are the Linear-Least-Squares Plot of the Data.

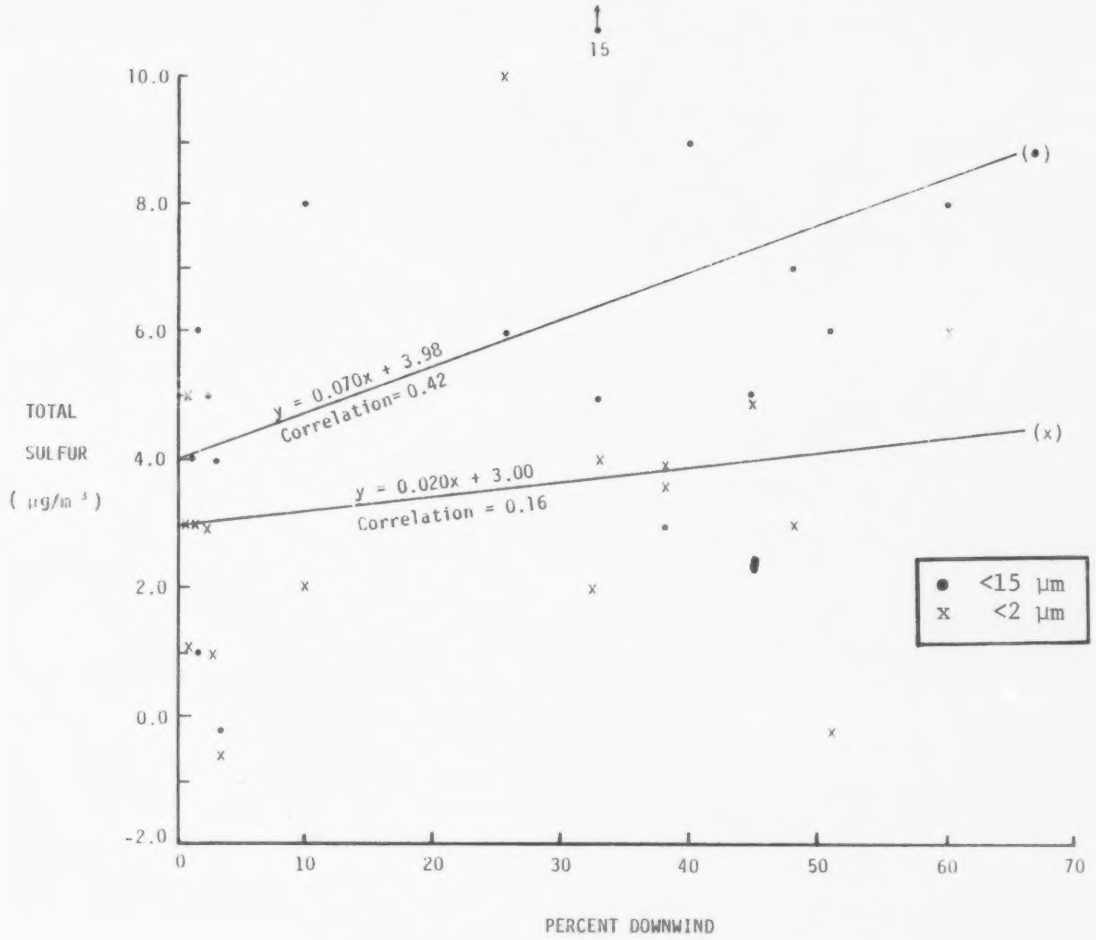


Figure 4-3. A Plot of the Total Sulfur in the <15 μm and <2.0 μm Particle Fractions versus Percent Downwind. The Lines are the Linear-Least-Squares Plot of the Data.

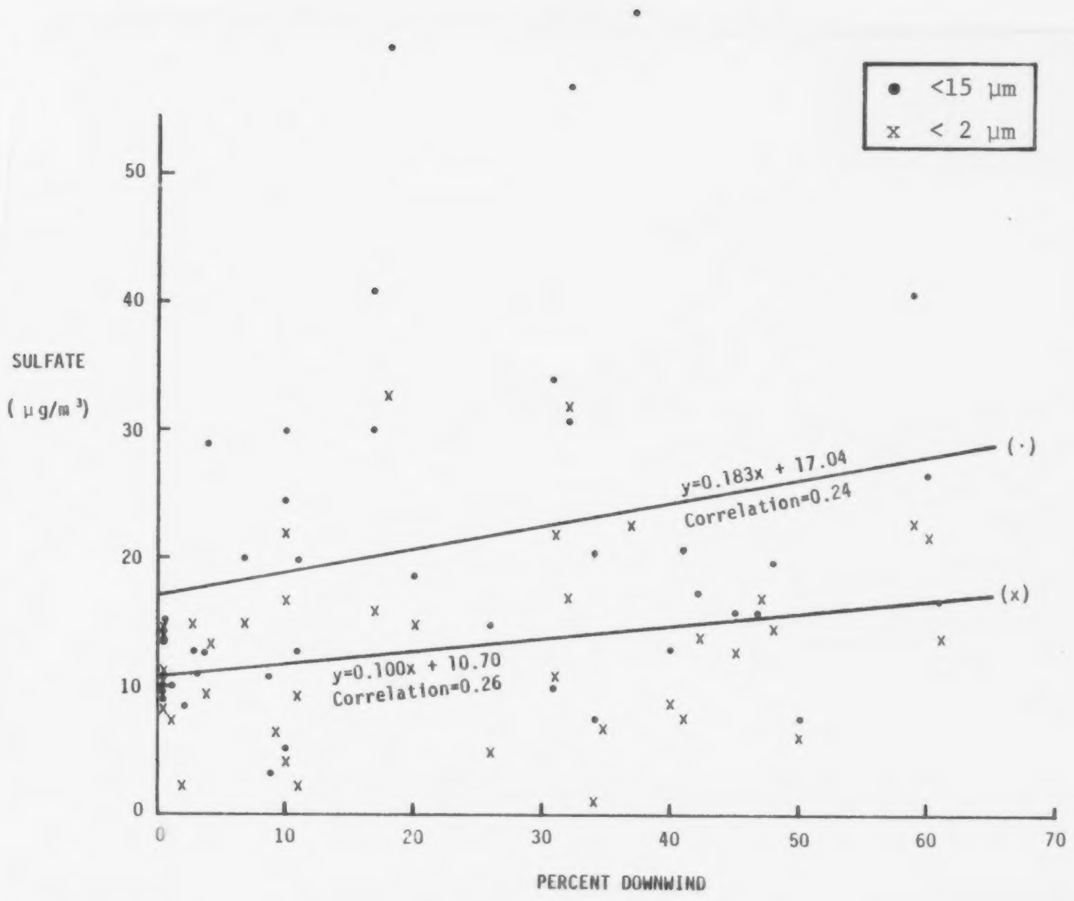


Figure 4-4. A Plot of the Sulfate in the <15 μm and < 2.0 μm Particle Fractions versus Percent Downwind. The Lines are the Linear-Least-Squares Plot of the Data.

For total sulfate:

<15 μm particles, $y = 0.183x + 17.04$
(correlation = 0.24, 39 points)

< 2 μm particles, $y = 0.10x + 10.70$
(correlation = 0.26, 39 points)

The total-to-fine ratio of total sulfur on particles was meaningless since total sulfur was not seen to increase in either size classification (very small slopes). For total sulfate, the ratio of increase (1.6) was nearly the same as the ambient ratio (1.8), but the small correlation coefficients associated with the linear least-squares plots imply that the data are nearly random, and conclusions drawn using these trends are very uncertain.

Analyses for sulfate suggest background sulfur values (from a percent of sulfate) of 5.68 μg/m^3 for <15 μm particles and 3.57 μg/m^3 for <2.0 μm particles. These values are significantly greater than sulfur values obtained from the total sulfur analyses.

Analyses for sulfate were performed using ion chromatography while analyses for total sulfur were performed using the flash vaporization technique. Other researchers* have observed a similar discrepancy in the results for sulfur using these two techniques. Nevertheless, the data are consistent within either analytical scheme and their use here as bases for identifiable trends and differences is considered justifiable.

It is apparent from an inspection of the other inorganic data (see Data Volume) that the concentration of the species (Na^+, NH_4+, Cl-, NO_3-, total nitrogen and hydrogen) does not increase as a function of percent downwind. A multi-element analysis (15 metallic elements) by ICAP spectroscopy of composited filter samples, composited into downwind/upwind pairs, also showed no consistent differences or concentration trends; see Table 4-4.

The LoVol filters used for the trace metal analysis were the remnants of the filters used for leaching and vaporization speciation (see Figure 3-1). They were the whole filter minus the circular cutouts, or about 40% of the particle laden area. In addition, the clean portion of the filter added another 7.56 cm^2 of filter substrate to the background. Thus, the particle laden area was only about one-third of the filter parts digested for instrumental elemental analysis.

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*Hegg, D.A., and Hobbs, P.V., Measurements of Gas-to-Particle Conversion in the Plumes from Five Coal-Fired Electric Power Plants. Atmospheric Environment, Vol. 14, pp 99-116, (1980).

TABLE 4-4. ELEMENTAL ANALYSIS OF COMPOSITED PARTICULATE SAMPLES BY ICAP

Days	Type	Percent Downwind	Concentration in Atmosphere ($\mu g/m^3$)														
			Al	B	Ba	Ca	Cd	Cr	Cu	Fe	Pb	Mg	Ni	Ag	Ti	V	Zn
5,6	total*	0.88	33	3.5	0.3	41	0.4	0.1	0.3	.44	3.4	34	0.4	0.02	0.3	0.1	0.9
5,6	fine †	0.88	26	3.2	0.2	31	0.3	0.1	0.3	.12	2.7	31	0.1	0.02	0.2	0.1	0.5
5,6	total	36.1	19	3.4	0.2	53	0.4	0.04	0.2	4.1	3.0	26	0.2	0.02	0.4	0.1	0.8
5,6	fine	36.1	25	4.1	0.2	43	0.4	0.1	0.2	1.1	2.6	30	0.1	0.02	0.2	0.1	0.5
7,8, 9,12	total	2.11	28	2.3	0.2	36	0.3	0.1	0.3	1.0	4.5	31	0.2	0.01	0.3	0.1	0.8
7,8, 9,12	fine	2.11	28	2.8	0.2	35	0.3	0.4	0.3	1.2	2.9	31	0.3	0.01	0.2	0.1	0.5
7,8, 9,12	total	35.4	23	3.5	0.2	55	0.3	0.04	0.2	4.2	2.1	26	0.2	0.01	0.3	0.1	0.5
7,8, 9,12	fine	35.4	21	3.9	0.1	42	0.3	0.2	0.2	1.6	1.5	25	0.1	0.01	0.1	0.1	0.3

*Total refers to the <15 µm aerosol fractions.

†Fine refers to the <2µm aerosol fraction separated in a cyclone precollector [Southern Research Institute - Cyclone II, ESTHAG 13(11) 1387-1392 (1979)].

NOTE: All upwind or downwind (from several sites or time intervals) samples for two or four days were composited for analysis. Due to large average filter blank corrections, especially for Al, Ca, Fe, Mg, and Na (which produces negative values), the absolute values are somewhat tenuous, however, trends seen within each element may be considered valid.

The substrates are high in certain trace metal content, most notably Al, Ca, Fe, Mg and Na. The ICAP method frequently gives poor results for Na, and, in this case, most of the net values were negatives (not included in table). The other elements, whose cumulatives total mass exceeds the total particle loading, are believed to be inaccurate due to large filter blank corrections (average blanks were used). However, these data are herein used only to establish trends for separate elements. The precision of the data (reproducible to ± 10%) is considered good enough that relative values and trends are believed to be valid.

A strong correlation existed for total carbon versus percent downwind; see Figure 4-5. For total carbon:

<15 μm particles, $y = 0.676x + 11.0$
(correlation = 0.82, 15 points)

< 2 μm particles, $y = 0.308x + 7.58$
(correlation = 0.79, 15 points)

In addition, the ratio of carbon on the fines (i.e., <2 μm) to carbon on all particles decreases significantly as the percent downwind parameter increases. For all points below 10 percent downwind, this ratio averages 79.3 percent with a standard deviation of the mean of 3.7; the intercept ratio of 68.9. The approximate ratio at 50 percent downwind is about 51 percent. The ratio of the slopes indicates that of the additional particles (above background) collected at the downwind sites, only 46 percent of the carbon was in the <2 μm size range.

Thus, it appears that a much higher percentage of carbon was collected in the atmospheric sampling downwind of the plant and that the additional carbon was predominantly on particles greater than 2 μm in diameter. The upwind or ambient ratio of about 70 - 80 percent of the carbon on the fines definitely indicates a different origin from that being collected downwind. Generally, particles larger than 2 μm have a mechanical origin.

4.3.3 Data Correction for Site-Specific Factors

There is one major subtlety that must be addressed. Site #4 was the predominantly downwind site and recorded the consistently highest particulate loadings. However, in the immediate vicinity of Site #4 was a coal conveyor and two railroad tracks which were situated between the plant and the sampling site. Therefore, sampling Site #4 would collect emissions from the plant, conveyor, and trains. The main railroad track was very heavily used; 27 diesel and 21 steam trains were scheduled daily, almost uniformly around the clock. The other track was used by an electric train that transported coal from the mine to the plant.

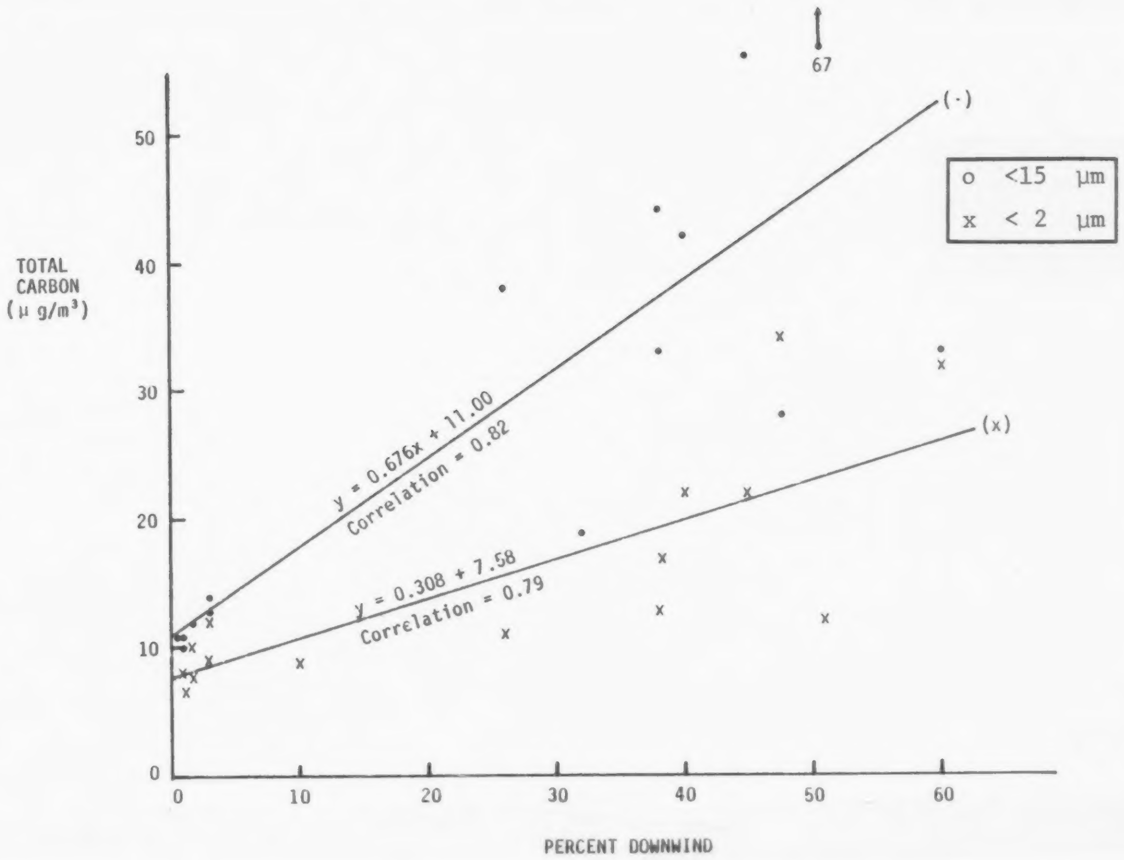


Figure 4-5. A Plot of the Total Carbon in the <15 μm and <2 μm Particle Fractions versus Percent Downwind. The Lines are Linear-Least-Squares Plot of the Data.

In an attempt to correct for any possible contributions at Site #4 from sources other than the gasification plant, a further specialized data analysis was carried out. The intent of this analysis was to see if a correlation between particulates and percent downwind truly exists, and to insure that it is not an artifact of the special conditions at the primary downwind site (Site #4). An analysis of <15 μm aerosol data for Site #4 and Sites #1, #2, #3, and #5 was made independently. The results are presented in Table 4-5.

To estimate the site-specific correction at Site #4, the natural (or upwind) <15 μm particle fraction was compared with the natural (or upwind) <15 μm particle fraction at Sites #1, #2, #3, and #5 (see Table 4-6). When Site #4 was upwind, the natural loading was 150 $\mu g/m^3$, while all other sites averaged 62 $\mu g/m^3$ natural loading. This 88 $\mu g/m^3$ may be attributed to local aerosol pollution sources in the immediate vicinity of Site #4.

A crude correction of Site #4 values was made by subtracting 88 $\mu g/m^3$ (the value attributed to local factors). In principle, a more sophisticated correction analysis would be possible but the statistical scatter of the data do not justify any further "fine tuning". Similar results were obtained for the <2 μm particle data.

Another way to determine whether the site-specific factors at Site #4 biased the data to a point where the conclusions might be different, is to compare the aerosol mass loading at Site #4 with those at Sites #1, #2, #3, and #5.

The results are:

Site #4	$y = 2.35x + 166$	(28 points) correlation = .44
Sites #1, #2, #3, #5	$y = 3.67x + 63$	(119 points) correlation = 0.52

where y = aerosol mass loading ($\mu g/m^3$)
x = percent downwind

The statistical interpretation of these equations indicates that there is a trend with 98% certainty for Site #4 and for all other sites a >99.9% certainty.

These results are similar in slope and correlation to other methods of analysis; see Figure 4-6, and confirm the trends already seen. For example, if the 88 $\mu g/m^3$ background is removed from Site #4 equation above, then

$y = 2.35x + 78$
correlation coef. = 0.44

TABLE 4-5. PERCENT CONTRIBUTION OF EACH SPECIES TO TOTAL PARTICULATE CATCH

SITE	COLLECTION FRACTION	TOTAL PARTICULATE (μg/m^3)	TOTAL CARBON (%)	TOTAL HYDROGEN (%)	TOTAL NITROGEN (%)	TOTAL SULFUR (%)	Na^+ (%)	NH_4^+ (%)	Cl^- (%)	NO_3^- (%)	$SO_4^=$ (%)
4	< 15 μm	230.8	18.46	2.22	0.87	2.64	-0.22	0.87	1.20	0.52	9.23
4	< 2 μm	89.7	22.74	0.98	1.34	5.00	-0.69	2.03	2.79	0.69	15.72
1,2,3,5	< 15 μm	83.6	9.21	3.32	1.72	5.31	0.18	2.85	2.75	1.20	25.24
1,2,3,5	< 2 μm	29.8	18.12	6.71	5.37	5.70	-2.16	8.26	7.05	-1.00	39.60

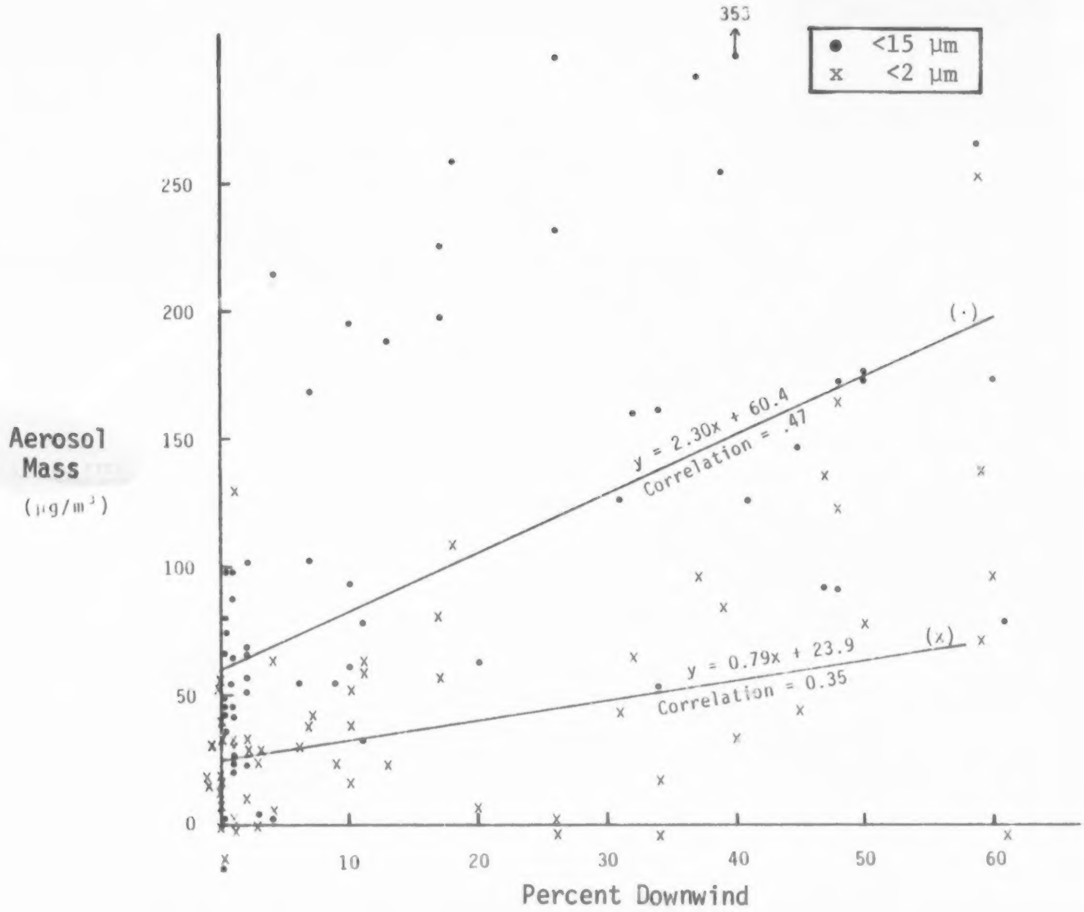


Figure 4-6. A Plot of the <15 µm and <2.0 µm Particle Fractions Corrected for Site-Specific Factors at Site #4 versus Percent Downwind. The Lines are the Linear-Least-Squares Plot of the Data.

which is not significantly different from

$$y = 2.30x + 60$$
correlation coef. = 0.47

as given in Figure 4-6.

4.3.4 Scanning Electron Microscopic Analysis of Particulate Matter

Upwind and downwind LoVol filters were selected for viewing by SEM; also several extra filters from Site #4 (the main downwind site, but perhaps affected by unusual local circumstances) were chosen.

The upwind samples clearly showed a much lower particle loading than the downwind samples. The catch on both samples looked similar in overall composition. That is, all <15 μm particle catches consisted of largely mineral material, composite in appearance. Although some fly ash was identifiable in the downwind samples, scattered fly ash was also seen in the upwind samples.

TABLE 4-6. INDEPENDENT ANALYSIS OF PARTICULATE CATCHES AT SITE #4 AND ALL OTHER SITES (#1, #2, #3, and #5)

Percent Downwind	Size Fraction	Site 4 *	1,2,3,&5	Difference
<10	< 15 μm	150 (4)	62 (63)	88
<10	< 2 μm	75 (5)	22 (63)	53
>10	< 15 μm	236 (24)	134 (41)	102**
>10	< 2 μm	104 (25)	52 (41)	52

*Average concentration in $\mu g/m^3$.

**Since only 4 and 5 points were available for Site #4, <10 percent downwind averages, those numbers must be regarded with far less confidence. Other standard deviations were about 10 - 15 percent. It has been noted that the contribution of site-specific factors at Site #4 may also be wind direction dependent. However, data from Site #4 is not considered sufficiently precise to warrant further quantitation of the effect of wind direction.

( )= Number of samples.

The composite mineral matter in the downwind micrographs could be from deposition, condensation or growth of crystals on fly ash; certain clusters had an approximately spherical appearance. However, some of the upwind clusters were similarly spherical, and it would be impossible to attribute with any certainty these rough-surfaced particles to fly ash. Typically fly ash takes the form of a smooth (amorphous), well defined sphere, some of which were present along with the approximately spherical clusters. Thus, one must conclude that fly ash contributes very little (less than 1 percent by weight) to the <15 μm particle catch.

The filter trapping the <2.0 μm fraction showed a much smaller size distribtuion, confirming the proper functioning of the cyclone precollector. Almost nothing larger than 2 μm was seen. Occasional spores and pollen grains were seen on the <15 μm particle catches.

However, the overwhelming quantity of material on both upwind and downwind filters was conglomerate, mechanically formed clusters (i.e., no evidence of being formed in high temperature processes) up to 15 μm in diameter. A possible source of the additional downwind loading is coal dust. The coal has a very high mineral (ash) content (20%), and may resemble the naturally formed, ambient dust found in the area.

4.4 ORGANIC ANALYSIS AND QUALITY ASSURANCE RESULTS

The results of the organic analysis and quality assurance programs are presented under three headings below:

- validation of methods for sample storage, preparation, and analysis,
- analysis of the organic compounds in the ambient air samples and in the coal gasification plants' by-products, and
- characterization of the Kosovo coal gasification plant's emissions profile and comparison with some ambient level goals (e.g., AMEG's).

The types of samples selected for screening, analysis and methods validation were as follows:

- solvent and apparatus blanks,
- sampling media blanks: HiVol filters and Tenax resin,
- spiked sampling media blanks: HiVol filters and Tenax resin aliquots spiked with selected aromatics,

- aerosol samples: loaded HiVol filters, front and rear Tenax vapor trap cartridges, and
- gasification by-products: middle oil and tar extracted or diluted in organic solvents.

An overview of the prioritized set of ambient air samples actually prepared and analyzed is shown in Table 4-7. Some studies conducted with spiked blank Tenax resin are not represented in this table, but are discussed below.

4.4.1 Validation of Methods for Sample Storage, Preparation, and Analysis

Tenax Vapor Trap Resin Homogenization--

The achievement of homogeneity in the mechanical mixing of the Tenax resin was verified experimentally by performing replicate analyses of several aliquots by thermal desorption GC-FID. Table 4-8 shows the results of analysis of two replicate aliquots of a Tenax resin sample (#1029, Day 5, Site #4, front trap). The agreement indicates a high degree of uniformity in this sample of homogenized Tenax resin.

Analyses Blanks for Solvent Extraction of Tenax Resin and HiVol Filter Samples--

In order to determine the background contribution in the analytical methodology, solvent and media blanks were prepared. Solvent blanks consisted of concentrated aliquots of the extraction solvents. The GC-FID chromatogram (Figure 4-7) shows the background peaks in cyclopentane, the Tenax extraction solvent, when concentrated 25:1. The large interfering background peaks are earlier than approximately 6 minutes retention time. This background chromatogram was significantly cleaner than that of n-pentane or diethyl ether, and was acceptable for the analysis of toluene (RT 6 minutes) and all heavier vapors extracted from the Tenax.

A portion of the HiVol filter solvent, methylene chloride, when concentrated 500:1, also showed a series of large, early-eluting background peaks before about 3.5 minutes (Figure 4-8). Figure 4-8 also shows some smaller peaks in the range, 8.5 to 10.5 minutes. These later solvent blank peaks did not interfere with the GC-FID analysis of the HiVol filters since the sample peaks had longer retention times.

In addition to solvent blanks, media blanks consisting of extracts of blank Tenax resin and HiVol filters were prepared according to the procedure given in Section 3. The GC-FID analysis of the Tenax blank showed background peaks from about 8 to 11 minutes. However, sample contributions were clearly discernable. The chromatograms in Figure 4-9 and 4-10 show the GC-FID analyses of a blank resin extract (#1153) and a sample extract (#1022, Day 6, Site #4 front cartridge).

TABLE 4-7. SUMMARY OF AEROSOL SAMPLES AND GASIFICATION BY-PRODUCTS PREPARED AND CHARACTERIZED

				Extract to GC-				TD-GC-	
Sample Identity (1)	Sample Number	Site Number	Solvent (2)	FID	HECD-S	HECD-N	MS	FID	MS
			Day 5 Aerosol Samples						
HV	129	1	M				X		
TF	1073	1	P,C	X	X	X	X		X
FB	1028	1	P	X					
HV	131	3							
TF	1011	3	C	X	X				X
TB	1002	3							
HV	132	4	P	X	X	X	X		
TF	1029	4	P,C	X	X	X	X	X	X
TB	1045	4	P				X	X	
			Day 6 Aerosol Samples						
HV	135	1	P	X	X	X	X		
TF	1010	1	C	X	X	X	X	X	X
TB	1067	1						X	X
HV	137	3	M	X			X		
TF	1037	3	C		X				
TB	1003	3							
HV	138	4							
TF	1022	4	C	X	X	X	X	X	X
TB	1046	4						X	X
			Day 7 Aerosol Samples						
HV	140	1	M	X	X				
TF	1088	1	C	X	X	X	X		
TB	1084	1	C	X		X			
HV	142	3							
TF	1048	3	C		X				
TB	1087	3							
HV	143	4	M	X	X	X	X		
TF	1069	4	C	X	X	X	X	X	X
TB	1047	4	C	X		X		X	
			Day 8 Aerosol Samples						
HV	145	1	M	X	X		X		
TF	1095	1							
TF	1089	3							
TF	1096	4						X	X

TABLE 4-7. SUMMARY OF AEROSOL SAMPLES AND GASIFICATION BY-PRODUCTS PREPARED AND CHARACTERIZED (Continued)

				Extract to GC-				TD -GC-	
Sample Identity (1)	Sample Number	Site Number	Solvent (2)	FID	HECD-S	HECD-N	MS	FID	MS
			Sampling Media Blanks						
HV Blank	114	-	M	X		X	X		
HV Blank	110	-	P						
HV Blank	111	-	P						
Tenax Blank	1044		C	X	X	X	X	X	
Tenax Blank	1053		C	X			X		
			Kosovo Coal Gasification By-Products						
Middle Oil	-	-	C,M	X	X	X	X		X
Middle Oil Base Extract	-	-	C			X	X		
Tar	-	-	M				X		
Heavy Tar	-	-	M				X		

Notes: 1. HV = HiVol filter, TF = Tenax front cartridge, TB = Tenax rear cartridge.

2. P = pentane, C = cyclopentane, M = methylene chloride, as solvents used in Soxhlet extraction of aerosol samples or for solution and dilution of gasification by-products.

TABLE 4-8. QUANTITATION OF DUPLICATE ALIQUOTS OF TENAX RESIN #1029 BY THERMAL DESORPTION GC-FID TO VERIFY SAMPLE RESIN HOMOGENIZATION

GC-FID Peak Number and Tentative Identification	RT* (minutes)	Aliquot 1 Peak Height	Aliquot 2 Peak Height
1. Benzene	14.5	54	56
2. Toluene	15.4	64	64
3. Ethyl benzene	16.5	11	17
4. Xylenes	16.9	26	32
5. Not Identified	18.0	31	34
6. Not Identified	19.6	42	47
7. Not Identified	21.8	25	27
8. Naphthalene	23.7	71	78
9. Not Identified	27.2	17	18
10. Not Identified	30.6	15	17
11. Not Identified	31.7	14	16
12. Not Identified	35.3	12	14
13. Not Identified	47.5	6.0	6.5

*Retention time on 50m nickel WCOT capillary column coated with Emulphora ON-870 used only in preliminary thermal desorption GC-FID analyses.

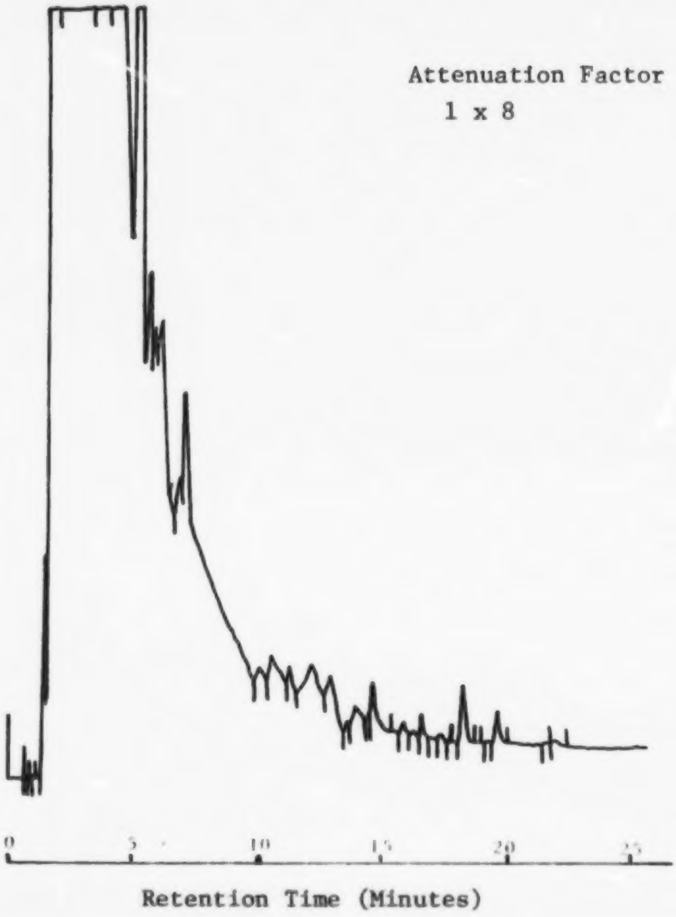


Figure 4-7. GC-FID Chromatogram of Tenax Extraction Solvent Blank; Cyclopentane, 25:1 Concentration

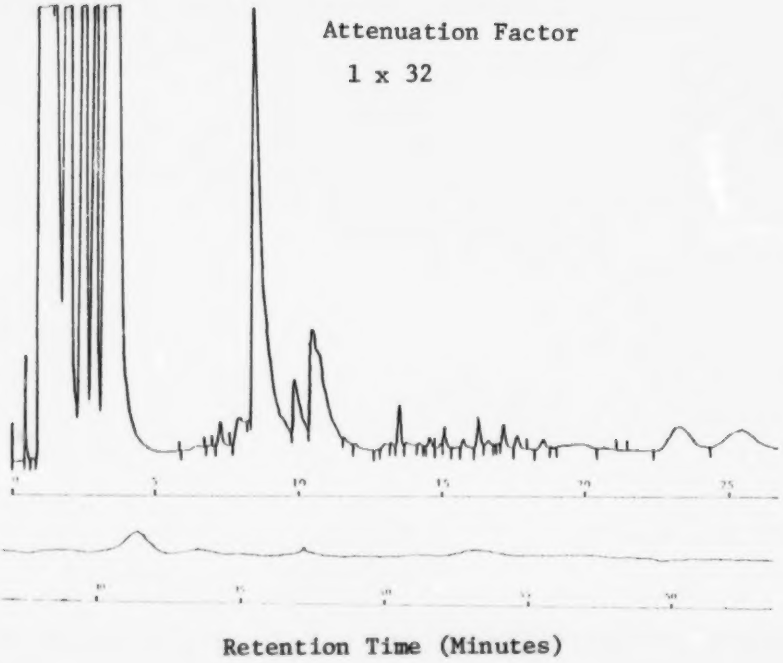


Figure 4-8. GC-FID Chromatogram of HiVol Extraction Solvent Blank; Methylene Chloride, 500:1 Concentration

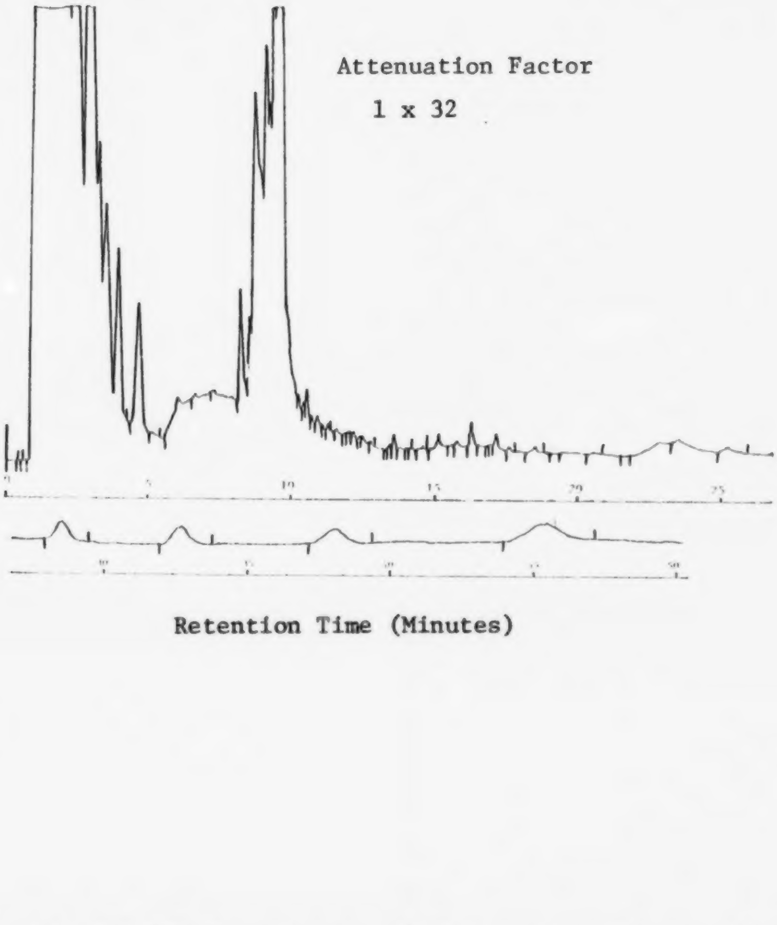


Figure 4-9. GC-FID Chromatogram of Cyclopentane Extract of Tenax Resin #1153 (Blank), Unspiked Concentrated 100:1

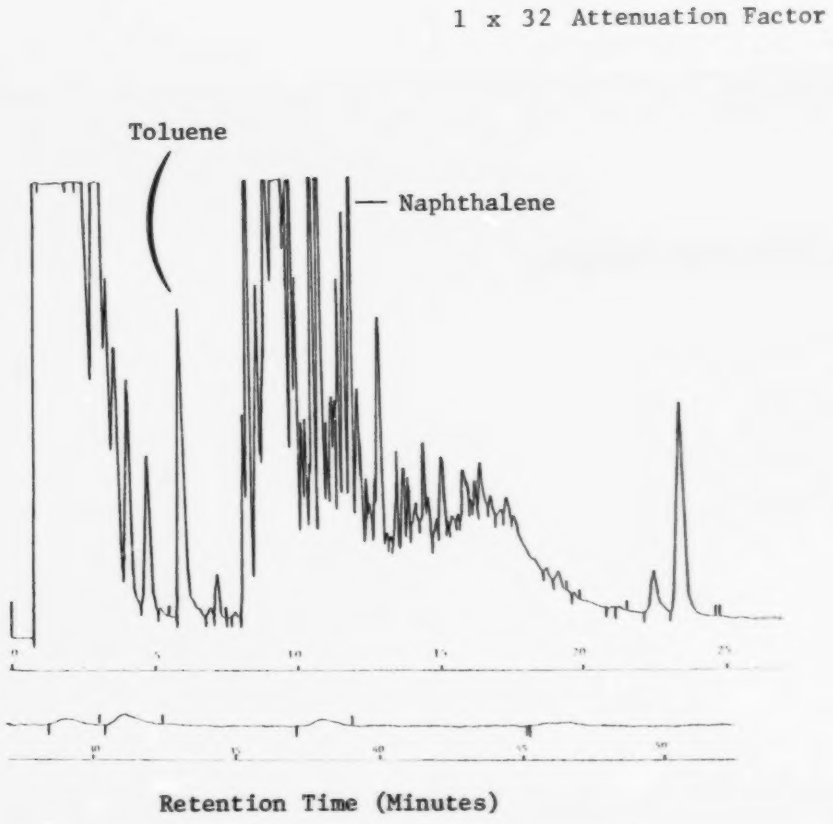


Figure 4-10. GC-FID Chromatogram of Cyclopentane Extract of Tenax Resin #1022 (Day 6, Site #4, Front), Spiked, Concentrated 100:1

The filter blank showed contributions from approximately 13 to 16 minutes and a large peak at approximately 29 minutes. Again, sample contributions were easily distinguishable. This is illustrated by the GC-FID analyses of a blank filter extract (#114) and a downwind filter extract (#143, Day 7, Site #4) shown in Figures 4-11 and 4-12, respectively. The difference is even more apparent when it is noted that the blank extract was four times more concentrated than the sample extract.

Solvent Extraction Efficiency--

The efficiency of the solvent extraction of the Tenax resin samples was measured in two experiments. In the first experiment, two 1.5 gram aliquots of blank resin were each spiked with approximately 10 mg of toluene, naphthalene, anthracene, 1,2-benzanthracene, and benzo(a)pyrene. A third aliquot was prepared without spiking, to serve as a control. After storing for 12 days at room temperature to allow the spiked compounds to establish equilibrium with the Tenax, the resin aliquots were extracted according to the procedure given in Section 3 and analyzed by GC-FID. Each extract was analyzed twice to produce an average recovery value. The mean recoveries, illustrated in Table 4-9, were calculated by comparing peak heights of the recovered peaks to peak heights of the same compounds in the spiking solution.

The recovery efficiencies were approximately 100% for all compounds, except toluene. The mean of the four recovery measurements over 100% was 112% with a standard deviation of 7%. The cause of this bias for recovery values <100% was not isolated. It is felt that the recovery is essentially quantitative for the four less-volatile PNA's studied here. The lower value for toluene (66% x 100/112 = 60%) is attributed to loss during the concentration step. Thus, toluene cannot be quantitatively determined by the extraction method, although naphthalene and heavier PNA's can be.

In addition to spiked blank Tenax recovery studies, the extraction efficiency for one Tenax vapor phase sample (#1096, Day 8, Site #4, front cartridge) was examined by thermal desorption. The chromatograms shown in Figure 4-13 show the results of the thermal desorption GC-FID analyses of the resin sample before and after extraction with cyclopentane. These results clearly confirm an extraction efficiency in excess of 90 percent for essentially all the species that may be thermally desorbed from the resin.

As a QA measure for individual samples, all resin and filter samples were spiked with d_8-naphthalene. This served as a control for quantitative analysis by GC-MS. If, for any reason, a sample was extracted with poor efficiency, this could be determined by the recovery of d_8-toluene and d_8-naphthalene in the extract. Recovery values for all Soxhlet extracted samples used in sample quantitation are given in Table 4-10. It can be seen that recoveries for the d_8-toluene spike were almost always less than that for the d_8-naphthalene spike. The naphthalene spike recovery was judged to be the best estimate of sample extraction efficiency and was the one used in subsequent quantitation of pollutant concentration.

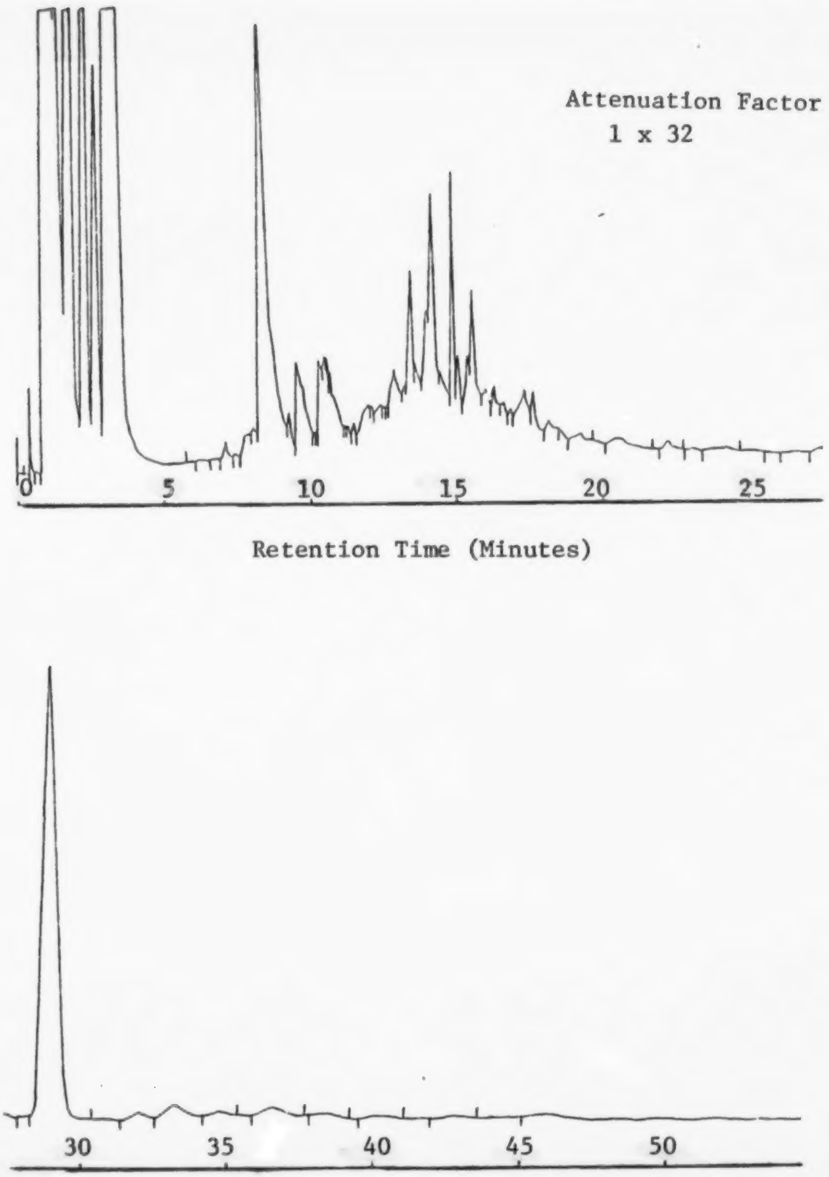


Figure 4-11. GC-FID Chromatogram of Methylene Chloride Extract of HiVol Filter #114 (blank), Concentrated 500:1 (The bottom figure is a continuation of the upper figure)

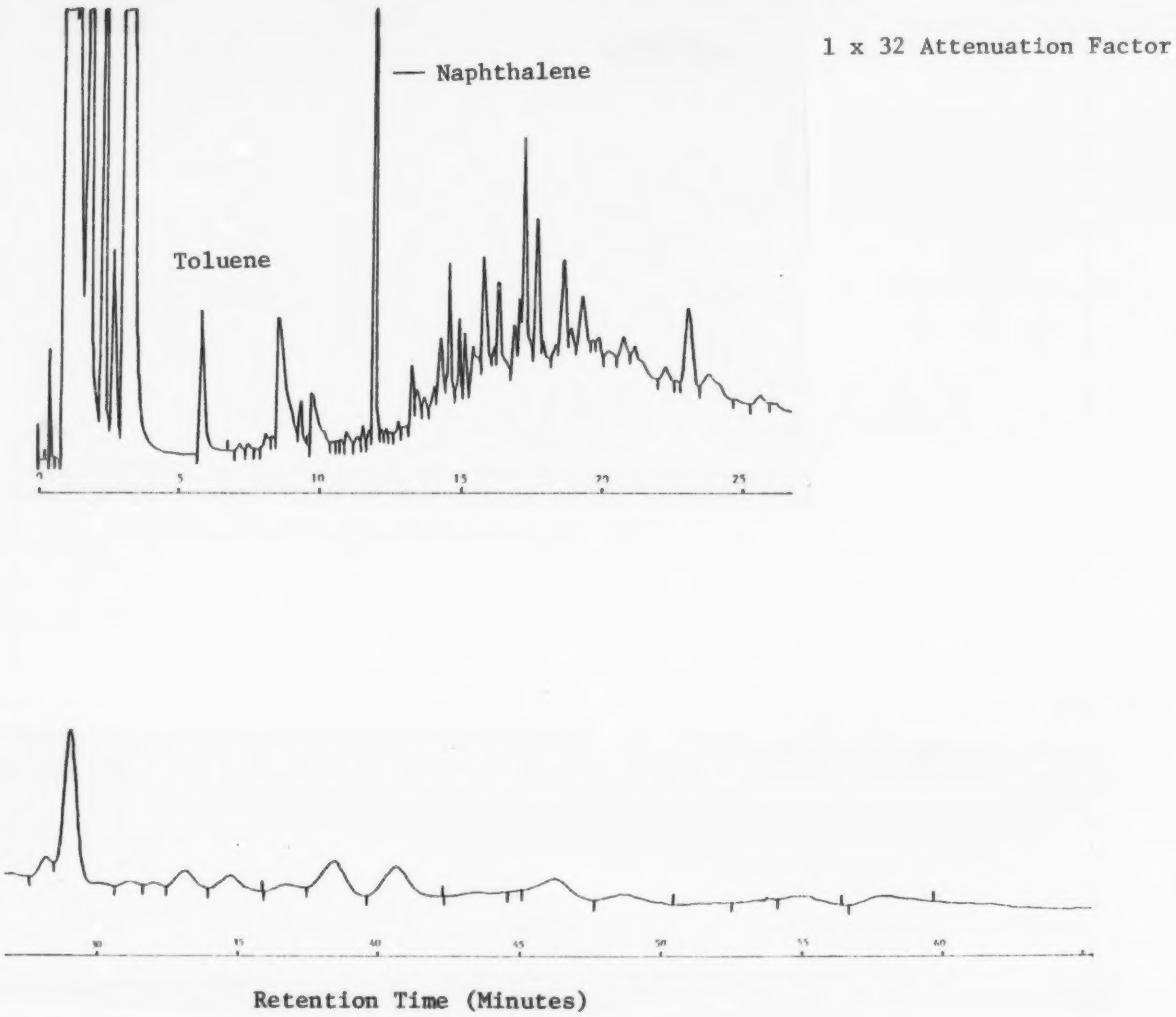


Figure 4-12. GC-FID Chromatogram of Methylene Chloride Extract of HiVol Filter #143 (Day 7, Site #4), Spiked, Concentrated 500:4 mL (The Bottom Figure is a Continuation of the Upper Figure)

TABLE 4-9. MEAN RECOVERIES OF FIVE AROMATIC COMPOUNDS SOXHLET EXTRACTED FROM SPIKED BLANK TENAX SAMPLES

Compound Identification	Mean Recovery*
d_8-toluene	66%
d_8-naphthalene	118%
d_{10}-anthracene	104%
1,2-benzanthracene	108%
Benzo(a)pyrene	119%

*Two 1.5 g Tenax duplicate blank samples were spiked with the PNA compounds and Soxhlet extracted for 24 hours with cyclopentane. The peak heights by GC-FID of the concentrated extracts were compared to those of the spiking solution to calculate the percent recoveries. All values shown are within a precision of ±15%. Mean of the four values >100% = 112%, while their standard deviation is 7%.

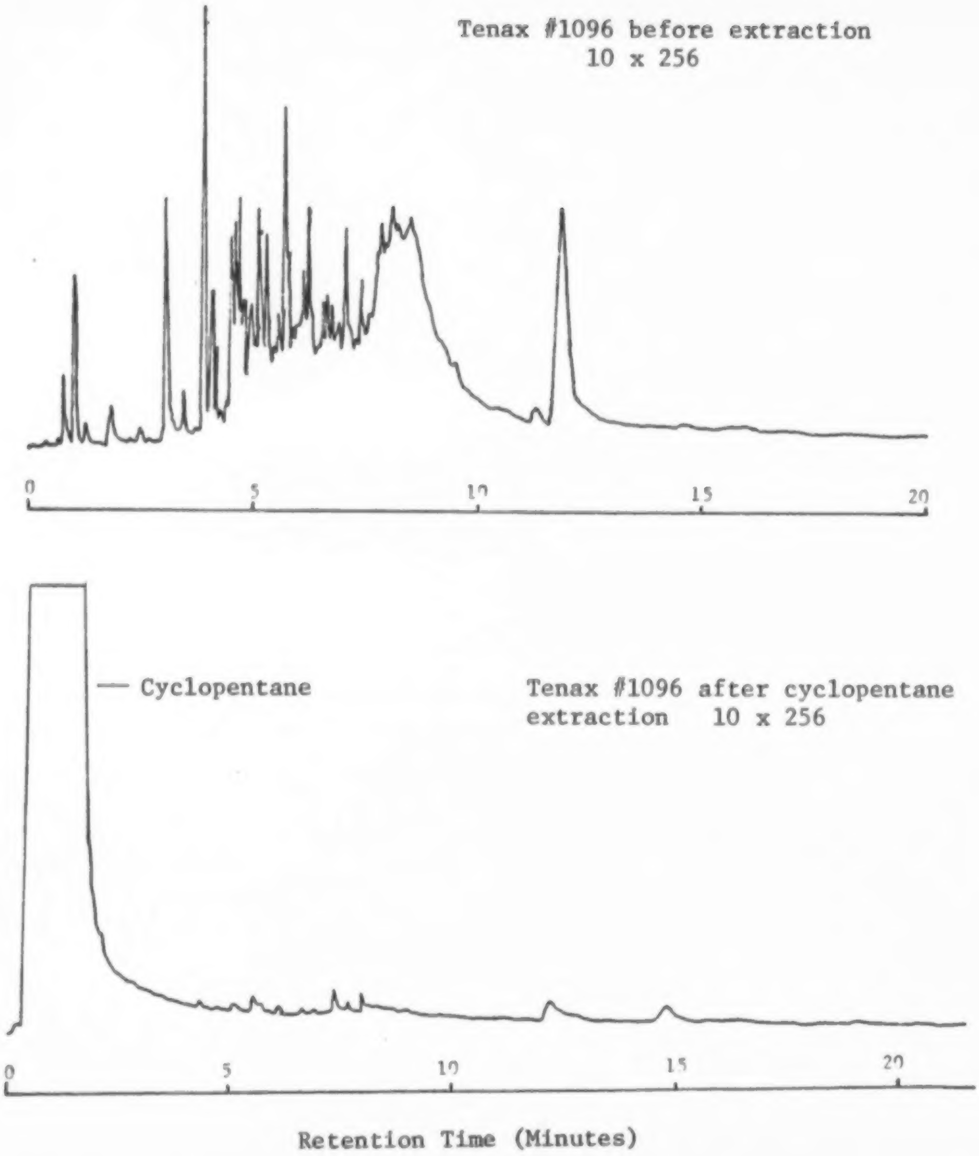


Figure 4-13. Thermal Desorption GC-FID Profiles for Tenax Vapor Phase Sample #1096 Aliquots Before and After Soxhlet Extraction with Cyclopentane

TABLE 4-10. SAMPLING DATA, ALIQUOT EXTRACTED AND SPIKE RECOVERY FOR AEROSOL SAMPLES USED IN QUANTIFICATION

Sample Number	Day/Site	Percent Downwind	Sample Volume (m^3)	Gross Sample Weight (g)	Weight of Aliquot Extracted (g)	Percent Extracted	Final Extract Volume (mL)	Percent Toluene Recovered[1]	Percent Naphthalene Recovered[1]
HiVol Filters									
114[2]	Blank	0.0	0.0	4.69	2.37	50.5	1.0		
129[2]	5/1	0.6	1617	4.75	2.31	48.6	4.0		
132	5/4	40.0	1417		All	100	1.0	11.7	43.2
135	6/1	1.0	1322		All	100	1.0	34.0	34.1
137	6/3	14.8	1639	5.09	2.60	51.1	6.0	115.5	92.9
138[3]	6/4	45.2	1476		All	100	None		
143	7/4	39.4	1608	5.27	2.74	52.0	4.0	28.0	72.8
144	7/5	1.3	1188	4.73	2.34	49.5	6.0	118.8	99.7
145	8/1	10.4	1126	4.80	2.30	47.9	1.0	14.6	52.0
Tenax Vapor Traps									
1010	6/1	1.0	4.39	2.48	1.00	40.3	0.5	58.1	81.5
1011[2]	5/3	18.7	5.52	2.84	1.49	52.5	0.5		
1022	6/4	45.2	5.53	2.51	1.00	39.8	0.5	145.3	202.2
1029	5/4	40.0	5.54	2.85	1.01	35.4	0.5	140.1	153.0
1044	Blank	0.0	0.0	2.62	0.39	14.9	0.5	52.5	86.5
1045[4]	5/4	40.0	5.54	2.60	0.40	15.4	1.0	31.4	83.2
1047[4]	7/4	39.4	5.55	2.66	1.60	60.2	0.5	127.1	102.2
1069	7/4	39.4	5.55	2.50	1.52	60.8	0.5	111.9	169.2
1073	5/1	0.6	5.70	2.57	1.00	38.9	0.5	57.0	81.2
1084[4]	7/1	0.7	4.20	2.35	1.52	64.7	0.5	60.8	99.2
1088	7/1	0.7	4.20	2.43	1.48	60.9	0.5	97.7	281.2
1096[2]	8/4	18.4	4.62	2.31	1.53	66.2	0.5		

[1] % recovery = apparent recovery = deuterated spike recovery + sample contribution. Note that for downwind Tenax samples (#1022, 1029, 1047, 1069) the Kosovo aerosol contribution to naphthalene was significant, leading to apparent recoveries >100%.

[2] Toluene and naphthalene were not quantified by GC-FID in these samples.

[3] Soxhlet apparatus malfunction caused sample loss.

[4] Rear Tenax vapor cartridge is equivalent to a field blank.

Gas Chromatographic Resolution of Aerosol Species--

The emphasis of Radian's analytical strategy was the use of multiple detectors (FID, MS, HECD-S, and HECD-N) following a single GC column to generate a series of chromatographic profiles where an equivalent retention time (RT) axis would provide an aid in chemical speciation. That is, a mass spectrometric identification of all trace components in the Kosovo atmosphere was not the objective, but rather the identification of enough components to characterize the aerosol and vapor samples. These identifications and the sulfur- and nitrogen-specific profiles provided sufficient data, in a cost-effective approach, to achieve an initial assessment of the coal gasification plant's impact on the ambient air downwind of the process emissions.

The specifications of the GC column appropriate for these objectives are:

- compatible for use with each of the different detectors, both sample media and all sample separation methods,
- resolution sufficient to separate the major isomeric groups that might be present,
- a temperature-programmable range to extend from benzene to the benzopyrene isomers in a single chromatogram, and
- ability to be prepared in Radian's laboratory, in a reproducible manner, in different configurations, as required for each instrument.

A packed GC column, 10% OV-101 on 80/100 mesh Supelcoport in 3 m (10') x 2mm ID nickel tubing, was found to meet these specifications for most of the analyses reported here. The only exception resulted from the poor peak shape this column gave for basic N-containing compounds. To provide better speciation for this class of compounds when detected by the HECD-N detector, another column was used: 10% Apiezon L, 2% KOH on 80/100 Chromosorb WAW in a 3 m (10') x 2mm ID glass column.

For both columns a similar temperature program was used:

50°C Hold for 5 minutes
20°C/minute from 50°C to 250°C
250°C Hold for 60 minutes

This program resulted in an elution time for benzene of approximately 4 minutes and for a standard of 1,2,5,6-dibenzanthracene approximately 70 minutes. Resolution was sufficient to differentiate ethyl benzene (bp 136.2°C) from the peak containing the p- and m-xylene isomers (bp 138.4°C, 139.1°C, respectively). The o-xylene (bp 144.4°C) was baseline resolved in all cases. Naphthalene eluted at a retention time of approximately 11 minutes on the OV-101 column and at approximately 15 minutes on the Apiezon L/KOH column.

Sample Vapor Breakthrough on Tenax Resin--

The Tenax vapor trap sampling rate of approximately 4 L/minute yielded a total air sample of approximately 6m^3 in the 24-hour sampling period. Sample vapor breakthrough was measured by quantitating corresponding components found in the front and rear Tenax cartridges. A downwind site (Site #4) sample set was selected since it was expected to exhibit the highest organic vapor loading and thus be more susceptible to breakthrough. The Tenax cartridge assembly for Day 6, Site #4 was used: Tenax #1022 front and #1046 rear.

Tenax aliquots were weighed and analyzed by thermal desorption GC-FID. Peaks at the same retention times in the two samples were quantitated by peak heights and corrected to equivalent aliquot weights. Complete breakthrough would be evidenced by equal concentrations of vapor in both the front and rear Tenax cartridges.

Table 4-11 shows the results of these measurements. Equivalent amounts of benzene and toluene were measured in the front and rear cartridges, these vapors then appear to have broken through completely under the Kosovo sampling conditions. About 15 percent of the total amount of the xylenes was found on the rear tubes and only about 2 percent of the naphthalene. It can be concluded that a small loss of the xylenes may have occurred, probably less than 10 percent, and that all heavier vapors were collected quantitatively.

This same result is shown graphically in a comparison of the thermal desorption GC-FID chromatograms of a front Tenax cartridge (#1029, Day 5, Site #4) shown in Figure 4-14 and its corresponding rear cartridge (#1045, Day 5, Site #4) shown in Figure 4-15. Only benzene, toluene and to a much lesser extent, the xylenes, are seen in the rear cartridge due to breakthrough.

Sample Vapor Storage Stability on Tenax Resin--

A study was conducted to measure the stability of sorbed aromatic compounds on Tenax resin when stored in the Radian laboratory under the same conditions as the aerosol samples. Replicate 0.05 g aliquots of blank Tenax resin were spiked with 100 ng each of the five following compounds: benzene, toluene, naphthalene, anthracene and 1,2-benzanthracene. Individual aliquots were analyzed in duplicate or triplicate by thermal desorption GC-FID on days 1, 21 and 32 of the storage period. The Tenax aliquots were stored in septum sealed 1 mL vials in the refrigerator until randomly selected for analysis.

TABLE 4-11. SAMPLE VAPOR BREAKTHROUGH: QUANTITATION BY GLC-FID OF CORRESPONDING COMPONENTS ON A DOWNWIND FRONT-REAR TENAX CARTRIDGE SET

Tentative Peak Identification	Retention Time (Minutes)	Peak Height (mm)		Percent of Total Peak on Rear Cart.
		Tenax #1022 Front Cart.	**Tenax #1046** Rear Cart.	
1. Benzene	3.9	126	117	48%
2. C_7-alkane	5.1	40	27	40%
3. Toluene	6.5	1335	1243	48%
4. C_8-alkane	7.3	184	61	25%
5. Ethyl benzene	8.1	720	137	16%
6. p- and m-Xylenes	8.3	2420	289	11%
7. o-Xylene	8.7	608	110	15%
8. Naphthalene	12.4	980	19	2%
9. Methyl naphthalene	13.5	512	10	2%
10. Anthracene	18.0	128	6	4%
11. Methyl anthracene	18.9	35	2	5%
12. Unidentified	21.6	32	2	6%

*Values given are within ± 15%

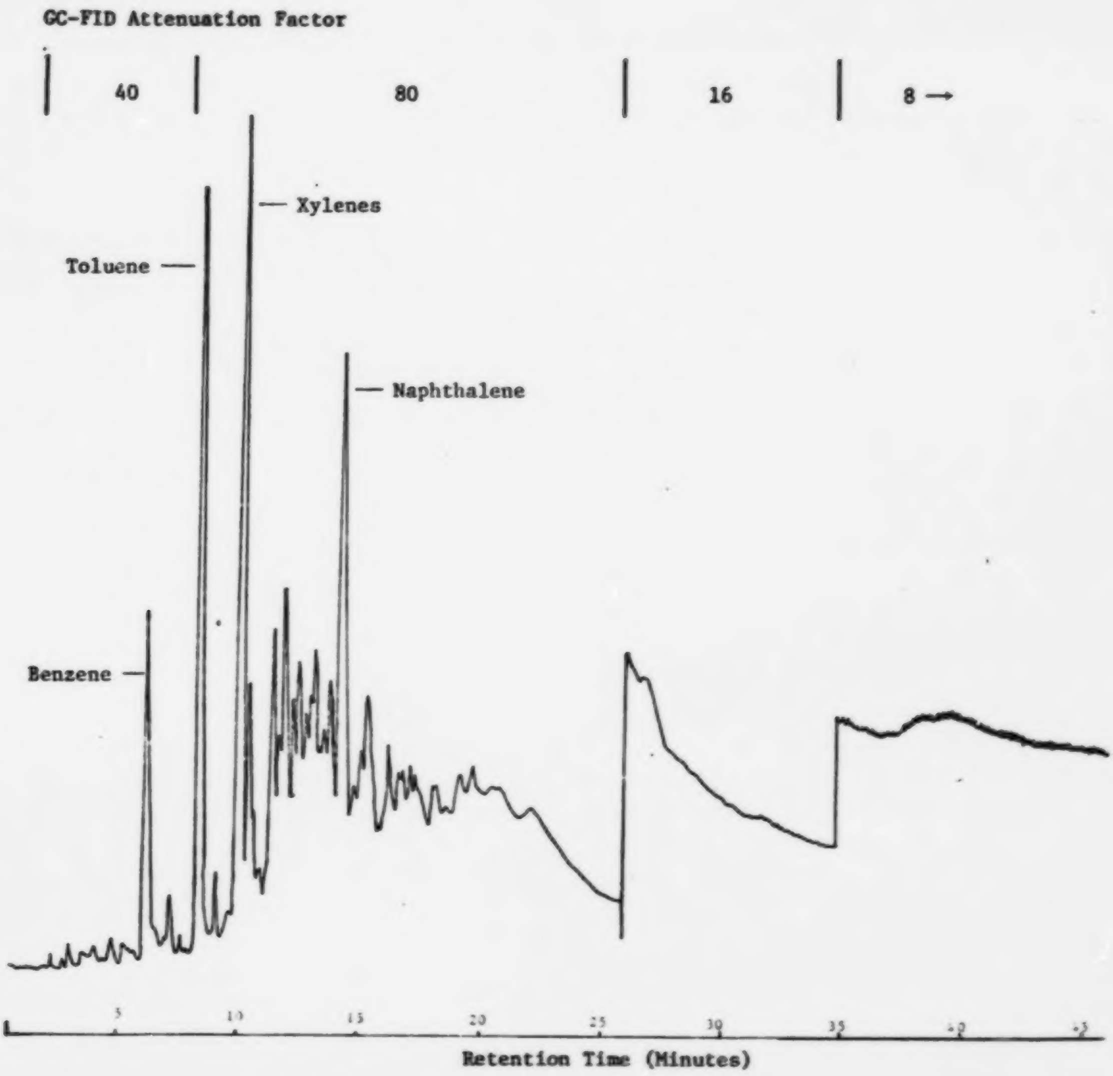


Figure 4-14. Thermal Desorption GC-FID Chromatogram of a Front Tenax Cartridge (#1029, Day 5, Site #4)

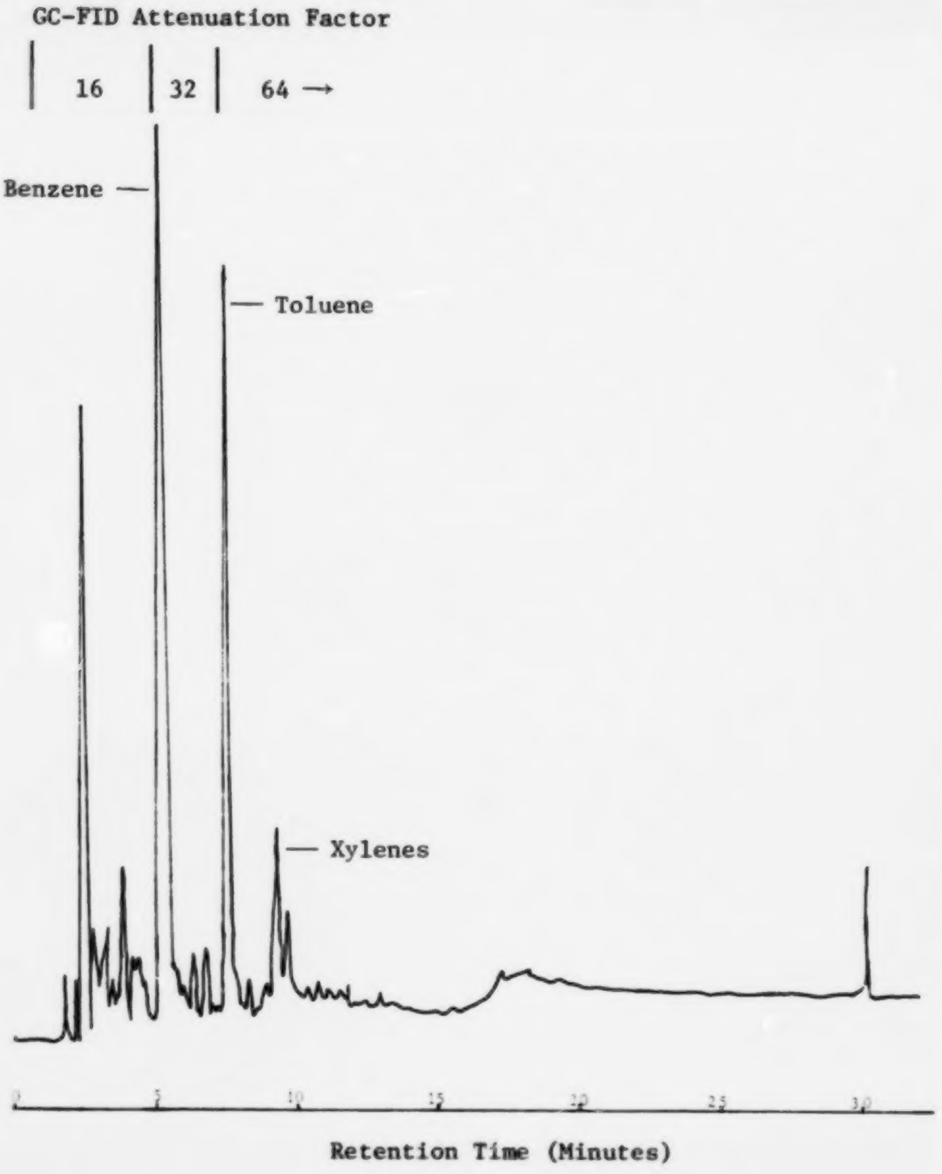


Figure 4-15. Thermal Desorption GC-FID Chromatogram of a Rear Tenax Cartridge (#1045, Day 5, Site #4)

Recovery of each compound was calculated by comparing the individual peak height with those produced by an analysis of the spiking standard. The graph of percent recovery versus storage time shown in Figure 4-16 shows that no trend of sample loss or gain occurred for sorbed compounds with the possible exception of 1,2-benzanthracene. It was concluded that, within the precision of the experiment, ± 15 percent, no systematic loss of the five sorbed aromatics occurred over almost five weeks of storage.

Thermal Desorption Blanks, Standards and Recovery Efficiency--

A thermal desorption GC-FID chromatogram of the blank Tenax resin in Cartridge #1044 (shipped to Kosovo, but returned without an air sample) is shown in Figure 4-17. The chromatogram shows a number of large peaks. Since system blanks and successively desorbed Tenax did not exhibit any significant background peaks, it was concluded that these peaks in Tenax #1044 were probably due to incomplete removal of the solvents that ORNL used to clean the Tenax. Actually, the Tenax from an upwind (Site #1), rear Tenax cartridge provided a much cleaner blank. The solvent residues were washed away by the $6m^3$ of sample air and the chromatogram showed at most only very small peaks for benzene and toluene.

Thermal desorption and GC conditions were developed and validated which would yield good resolution and a quantitative recovery for five aromatic compounds sorbed on the Tenax. Figure 4-18 shows a chromatogram for the compounds benzene, toluene, naphthalene, anthracene and benzanthracene spiked onto Tenax at the level of 100 ng each on 0.05 g resin from a cyclopentane standard solution. Chromatographic resolution was adequate for separating most aromatic isomer groups encountered in the aerosol samples.

Quantitative recovery of sorbed species by thermal desorption was measured for the same five aromatic compounds by two methods:

- comparison of GC-FID peak heights for the five standard compounds spiked onto Tenax or spiked into the empty sample tube and analyzed by the same thermal desorption cycle, and
- successive thermal desorption cycles for the same Tenax vapor aliquot to measure the quantity of sorbed species remaining after the first cycle.

The results of the comparison of peak heights is shown in Table 4-12, where the individual peak height measurements from replicate analyses are shown. The ratios of the mean peak heights indicates a thermal desorption recovery between 90 and 100 percent for these five compounds. A comparison of the chromatograms in Figure 4-19 supports this conclusion: essentially all of the sorbed organic vapors were removed in the first 10 minute cycle of thermal desorption at 250°C. The Tenax aliquot was removed from the heated thermal desorption injector between cycles.

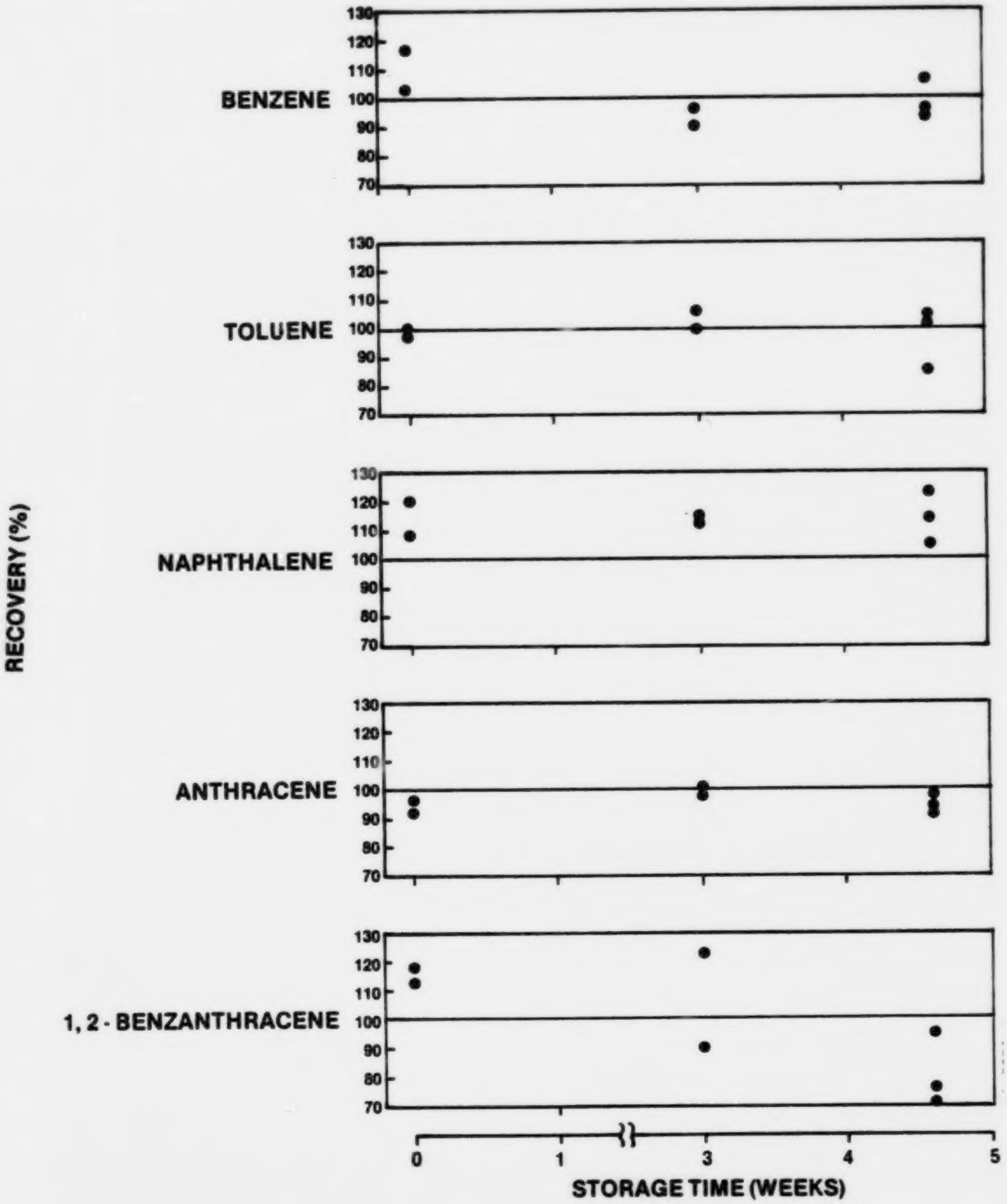
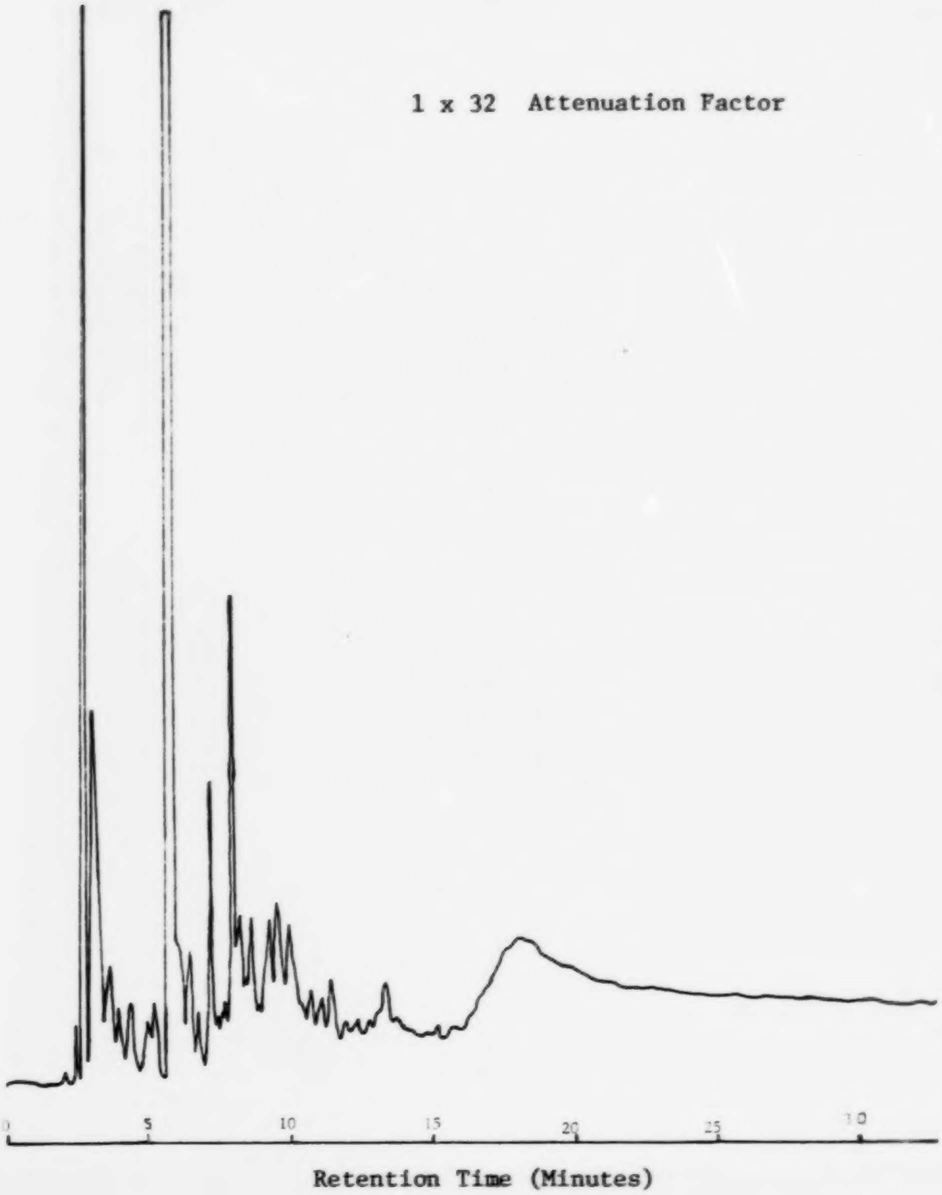


Figure 4-16. Recovery of Standard Compounds Sorbed on Tenax Resin as a Function of Storage Time



Fiugre 4-17. Thermal Desorption GC-FID Chromatogram for the Tenax Resin in Vapor Cartridge #1044, a Blank

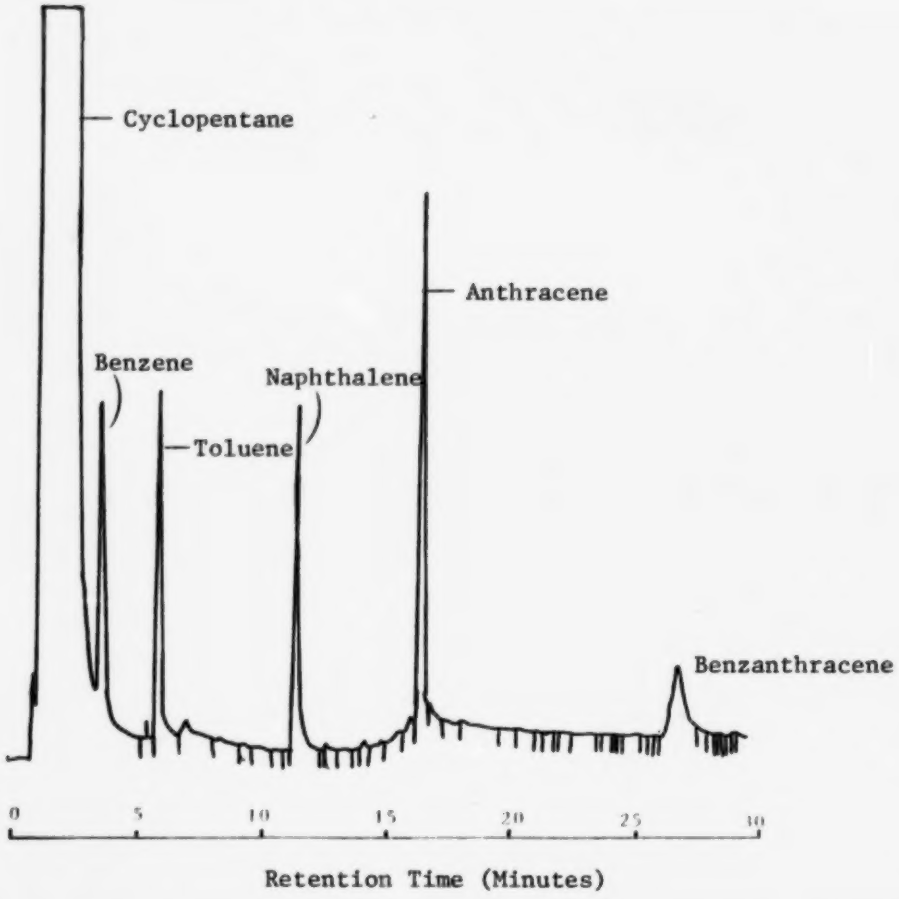


Figure 4-18. Thermal Desorption GC-FID Chromatogram of Blank Tenax Resin Spiked with Five Aromatic Compounds

TABLE 4-12. MEASUREMENT OF THERMAL DESORPTION RECOVERIES FOR FIVE AROMATIC COMPOUNDS SORBED ON TENAX RESIN

Method of Injecting Standard Mixture	Measured GC-FID Peak Heights (mm)[1]				
	B	T	N	A	BA
1. Direct injection of standard into thermal desorption inlet	--- 111 109	--- 108 113	120 108 119	146 138 148	19 16 33
1. Mean Peak Height = $\overline{PH_1}$	110	110	116	144	23
2. Injection of standard onto blank Tenax resin	110 88	98 103	113 100	139 131	28 25
2. Mean Peak Height = $\overline{PH_2}$	99	100	107	135	26
Recovery[2] = $\frac{\overline{PH_2}}{\overline{PH_1}}$	90%	91%	92%	94%	113%

[1] B = benzene
T = Toluene
N = Naphthalene
A = Anthracene
BA = Benzanthracene

[2] Estimated uncertainty in mean recoveries ± 15-20%.

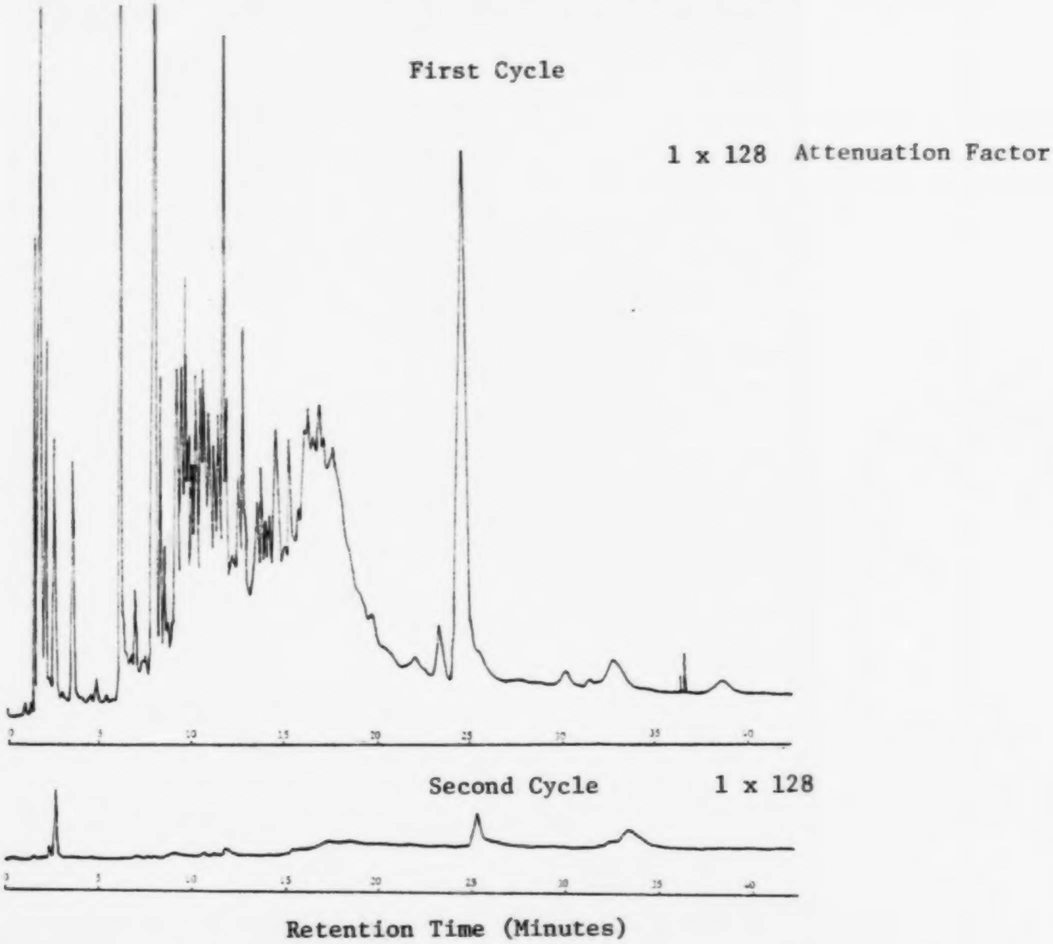


Figure 4-19. GC-FID Chromatogram of a Tenax Downwind Air Sample During Two Successive Thermal Desorption Cycles

The quantitative recovery by thermal desorption of compounds sorbed on Tenax covering such a wide range in volatility, i.e., benzene to benzanthracene, represents a significant improvement in this methodology and one of the important accomplishments of the Radian program in the organic analysis of the Kosovo samples.

4.4.2 Organic Analysis of Ambient Air Samples and Gasification By-Products

Profiles of Sulfur and Nitrogen Compounds--

The Hall Electrolytic Conductivity Detector (HECD) was able to selectively detect sulfur- and nitrogen-containing species in the air samples and some of the gasification plant's by-products. The application of this methodology yielded the following results:

- a positive correlation between the air samples and components found in the gasifier by-product, medium oil;
- a profile of the major sulfur- and nitrogen-containing species in the ambient air samples;
- profiles and tentative identifications as input to the GC-MS interpetation for positive identification of both sulfur-and nitrogen-containing species in the air samples; and
- relative quantitation of the major nitrogen- and sulfur-containing components using p-nitrotoluene and thiophene, as standards.

Sulfur Species--

Two representative profiles of the sulfur-containing species are illustrated in Figure 4-20. The chromatograms show the distribution of sulfur species in the medium oil from the gasifier and the downwind air sample #1022. The retention times are slightly different for the compounds due to variations in the initial temperature of the GC, but the profiles have a high degree of correlation.

The two large peaks at about 6.5 minutes in the medium oil were tentatively identified by spiking. The compounds, 2- and 3-methylthiophene, were spiked into the sample and the peaks which increased relatively to the others were identified as the spiked compounds. This technique was also used for thiophene (RT ∿3 min.), and 2,4-dimethylthiophene (RT ∿9 min), ethylthiophene (RT ∿9 min), and benzothiophene (RT ∿13 min.). Thiophene was not detected in the Texax sample, perhaps because of its high volatility and subsequent non-quantitative collection on Tenax resin.

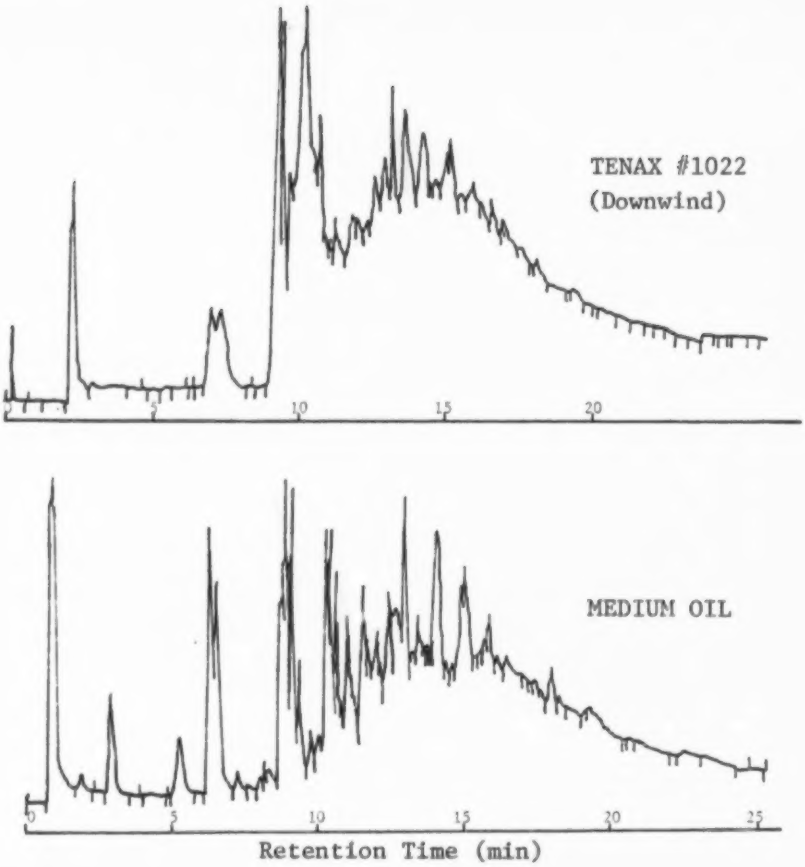


Figure 4-20. GC-HECD Sulfur Compound Profiles for a Downwind Tenax Vapor Trap Extract (#1022, Day 6, Site #4) and for Kosovo Medium Oil

The resin and/or solvent contained an interference which masked part of the profile around 10 minutes. The upwind site Tenax (#1010, Site #1) and the blank Tenax (#1044) sulfur profiles are given in Figure 4-21 and are essentially identical. That is, no sulfur species were detected in the upwind vapor sample corresponding to the downwind sample #1022.

Table 4-13 lists approximate concentrations of the sulfur compounds based on the response of thiophene. Even though the concentrations are very low at the sample site, the compounds present in the medium oil which could be trapped by the Tenax are found in the downwind samples. The upwind sample listed in Table 4-13 gave virtually no sulfur species above the detection limit of 0.005 $\mu g/m^3$ (about one part per trillion by volume) except the blank background peaks.

Nitrogen Species--

Very similar results were found with the nitrogen components in the medium oil by-product and the air samples. In Figure 4-22 the profiles of medium oil and a downwind sample are illustrated. The profiles are similar. However, the large, early peak in medium oil at 6.7 minutes is not present in the air sample. Again, this may indicate that the more volatile compounds were not trapped by the Tenax cartridge and/or were lost during solvent concentrations.

Most of the nitrogen compounds in the medium oil and the air samples appeared to be alkyl substituted pyridene(s) or quinoline(s), as identified by GC-MS. One of the peaks at about 15.7 minutes retention time and the peak at about 18.5 minutes retention time were also seen in the upwind samples but not in the blank resin (Figure 4-23). This indicated that the source of these compounds was not the gasification plant.

Table 4-14 contains the approximate concentrations of nitrogen species detected based on the response of 3-nitrotoluene. No N-containing species were detected on the HiVol filters. All the downwind samples contained low concentrations of many of the nitrogen compounds found in the medium oil. The upwind sample and the blank had none of these compounds except perhaps quinoline. The identification of pyridine, alkyl substituted pyridine(s), quinoline and alkyl substituted quinolines directly correlates the sampled air to the gasification plant emissions.

Characterization of Ambient Air Samples by GC-MS--

Selected Kosovo ambient air samples were subjected to qualitative and quantitative analysis by GC-MS, using the methods described earlier. Except where indicated below, all chemical speciation was based on thermal desorption of Tenax resin aliquots and Soxhlet extraction of HiVol filters.

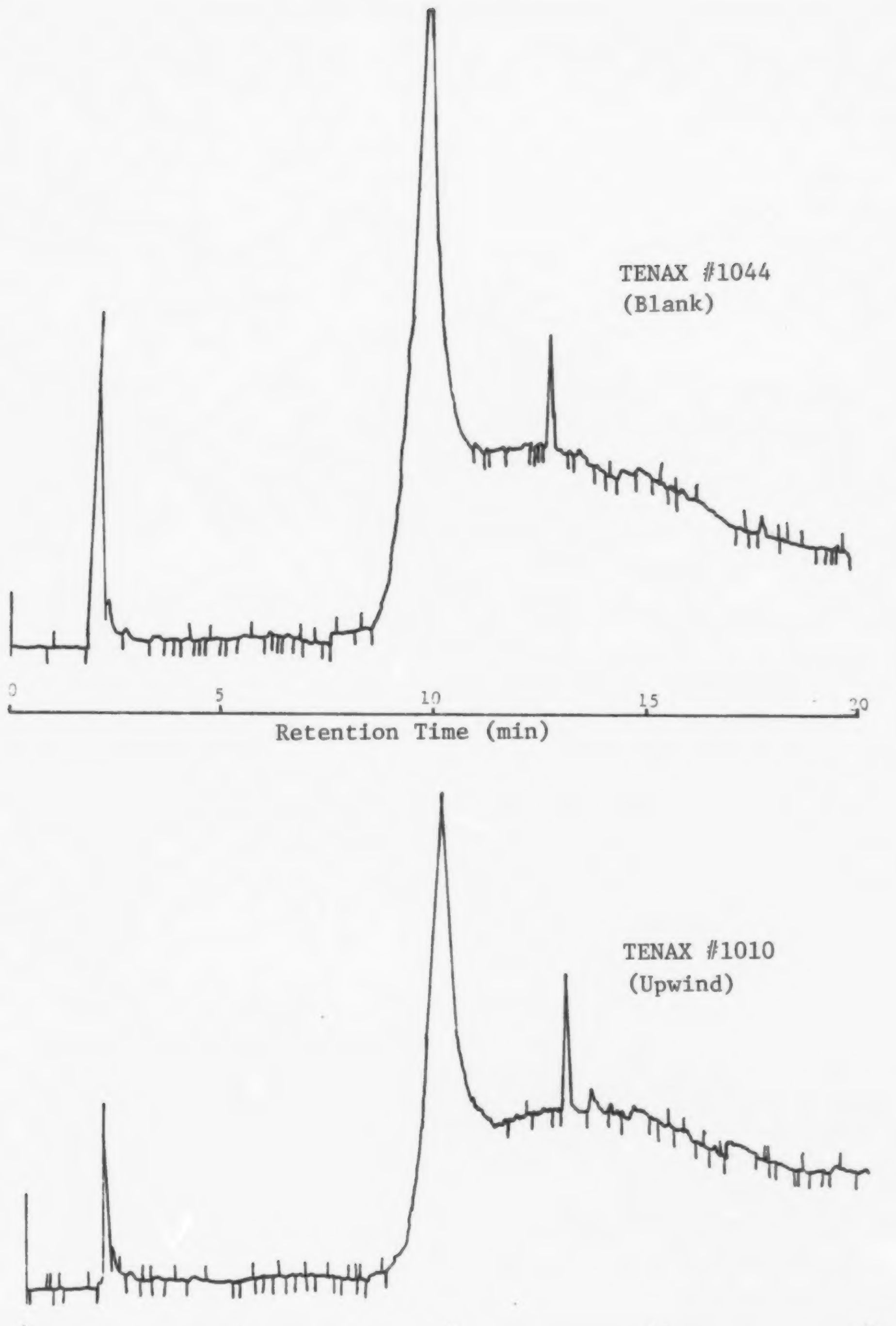


Figure 4-21. GC-HECD Sulfur Compound Profiles for an Upwind (#1010, Day 6, Site #1) and a Blank (#1044) Tenax Vapor Trap Extract

TABLE 4-13. TENTATIVE IDENTIFICATIONS AND APPROXIMATE CONCENTRATIONS OF SULFUR-CONTAINING COMPOUNDS IN KOSOVO VAPOR PHASE SAMPLES AND OF MIDDLE OIL BY-PRODUCTS

Compound(s)[1]	Medium Oil (By-Product)	1029 (Downwind)	1022 (Downwind)	1011 (Downwind)	1010 (Upwind)	1044 (Blank)	HVI35 (Upwind)	HVI32 (Downwind)
Thiophene	0.16 g/ℓ	<DL[2]	<DL	<DL	<DL	<DL	No peaks Detected	No peaks Detected
2-Methylthiophene	0.66	0.13 μg/m^3	0.04 μg/m^3	0.01 μg/m^3	<DL	<DL		
3-Methylthiophene	0.54	0.16	0.05	0.01	<DL	<DL		
2,5-Dimethylthiophene	0.21	0.18 (merged)	0.03	<DL	<DL	<DL		
Dimethyl- or Ethyl-thiophene(s)	0.42	0.07	0.10	0.007	ND[3]	ND[3]		
Dimethyl- or Ethyl-thiophene(s)	0.39	0.07	0.09	0.007	ND[3]	ND[3]		
Trimethyl- or Ethylmethyl-thiophene(s)	0.24	0.02	0.04	ND[3]	<DL	<DL		
Trimethyl- or Ethylmethyl-thiophene(s)	0.28	0.02	0.08	0.01	<DL	<DL		
Benzothiophene	0.34	0.02	ND (0.10)	<DL	ND[3]	ND[3]		
Methylbenzothiophene	0.42	<DL	0.12	<DL	0.005	<DL		

[1] Based on retention time of standards or boiling point.

[2] DL = 0.005 μg of Thiophene/m^3.

[3] Not detected due to interferences.

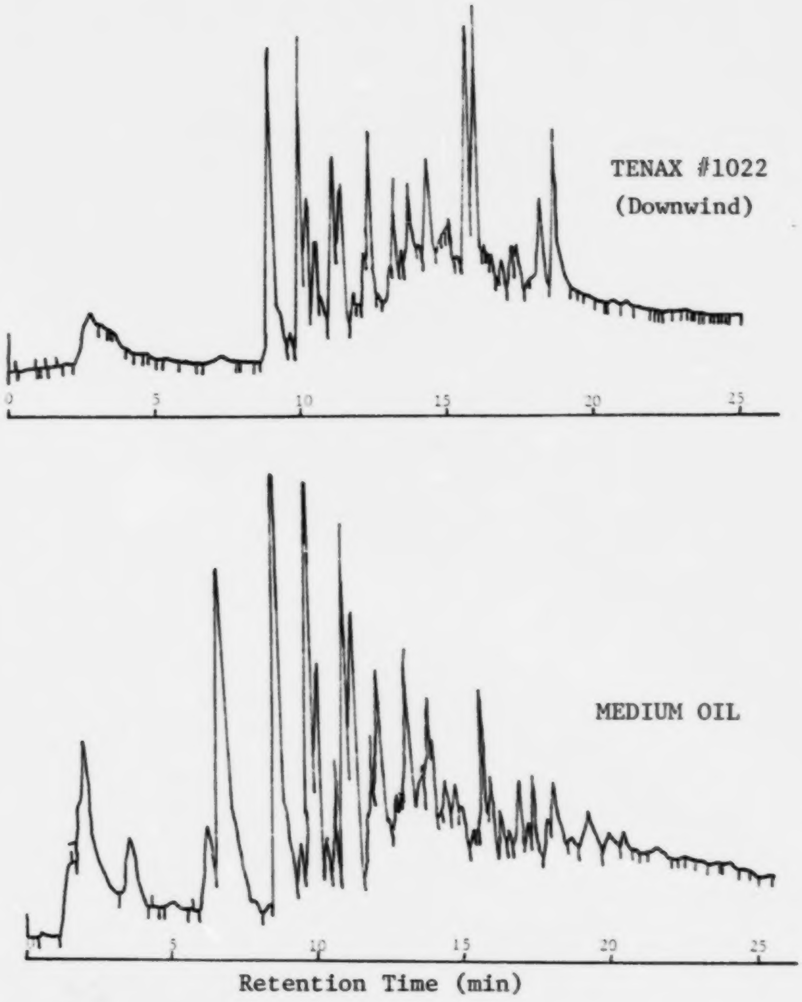


Figure 4-22 GC-HECD Nitrogen Compound Profiles for a Downwind Tenax Vapor Trap Extract (#1022) and for Kosovo Medium Oil

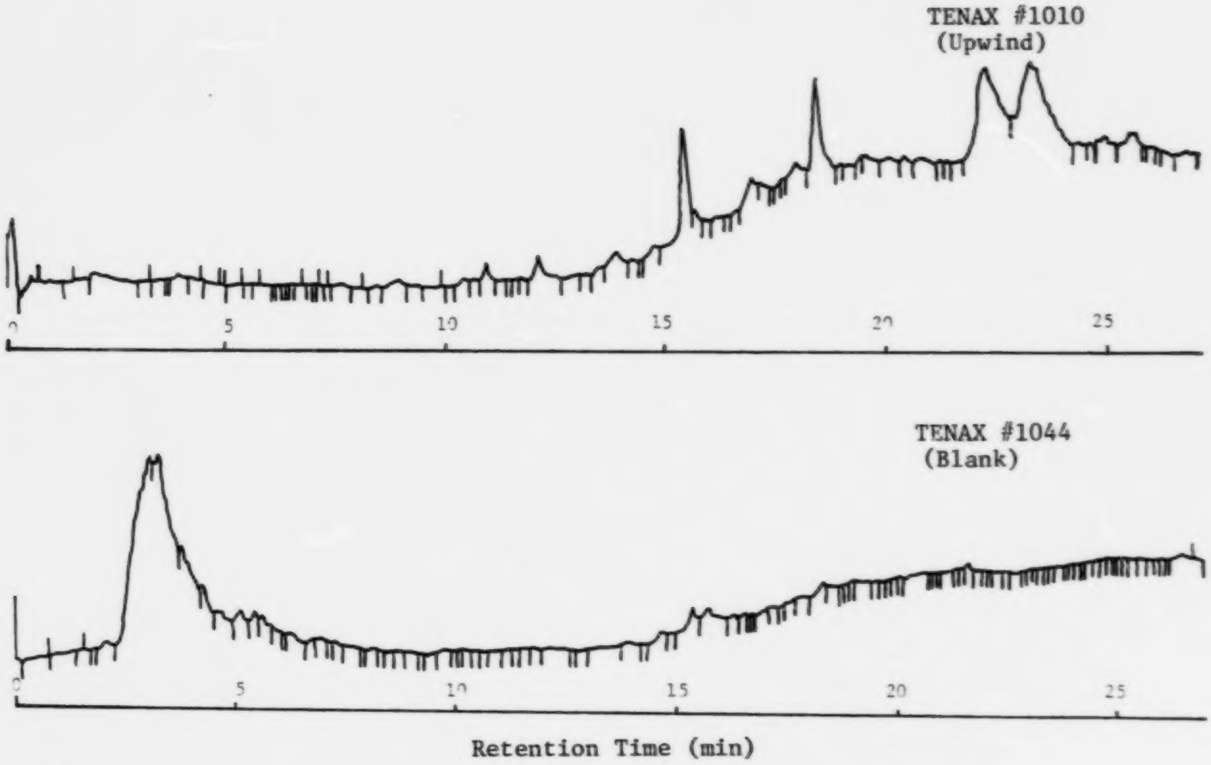


Figure 4-23 GC-HECD Nitrogen Compound Profiles for an Upwind (#1010) and a Blank (#1044) Tenax Vapor Trap Extract

TABLE 4-14. TENTATIVE IDENTIFICATIONS AND APPROXIMATE CONCENTRATIONS OF NITROGEN-CONTAINING COMPOUNDS IN KOSOVO VAPOR PHASE SAMPLES AND MIDDLE OIL BY-PRODUCTS

Compound(s)[1]	Medium Oil By-Product (g/L)	Downwind ($\mu g/m^3$)	Downwind ($\mu g/m^3$)	Downwind ($\mu g/m^3$)	Upwind ($\mu g/m^3$)	Blank[4] ($\mu g/m^3$)
Pyridine	5.4	<DL[2]	<DL	0.005 $\mu g/m^3$	<DL	<DL
2-Methylpyridine	4.2	0.36	0.62	0.04	<DL	<DL
3-Methylpyridine	2.9	0.19	0.55	0.04	<DL	<DL
Dimethyl- or Ethylpyridine(s)	2.3	0.21	0.46	0.11	<DL	<DL
Dimethyl- or Ethylpyridine(s)	2.3	0.17	0.49	ND[3]	<DL	<DL
Alkylpyridine(s)	0.99	0.20	0.56	0.06	<DL	<DL
Alkylpyridine(s)	2.6	0.11	0.46	0.02	<DL	<DL
Alkylpyridine(s)	0.71	0.16	0.74	0.11	<DL	<DL
Quinoline	0.72	0.46	0.94	0.21	<DL	0.13
Alkylquinoline(s)	0.69	0.19	0.54	<DL	<DL	<DL

[1] Concentrations of all compounds based on response factor for 3-nitrotoluene.
[2] DL = 0.005 μg 3-nitrotoluene /m^3.
[3] Not detected due to interferences.
[4] Concentration based on a hypothetical air sample of $5 m^3$.

Fourteen aromatic compounds or isomeric groups, including PNAs were selected to constitute a chemical profile of the gasification plant's major emissions for the purpose of comparing the ambient air samples from different sites and different days. Table 4-15 presents the profile of these fourteen compounds collected on Tenax vapor traps and HiVol filters at Sites #1, #3 and #4 on day 5. Table 4-16 presents the same profile for samples collected at Site #4 (the downwind site) for sampling days 5, 6, 7 and 8.

The profile presented in these tables has two principle elements:

- a relative quantitation of all detected peaks based on a 100% normalization to naphthalene in the Tenax samples of organic vapor and to anthracene in the HiVol samples of particulate matter, and
- an absolute quantitation (accurate to about a factor of 2) in $\mu g/m^3$ of air of the measured ambient level of naphthalene in the vapor and anthracene on the particulate.

The relative quantitation is based on the ratio of peak areas of the appropriate molecular ions listed in the table, as measured by GC-MS. Absolute quantitation is based on the methods of calculation discussed in Section 3, and involves the use of all of the following factors: instrumental response, extraction recovery, aliquot fractions, the volume of air sampled, the final volume of concentrated extracts, the concentration of deuterated internal standards, and GC-MS peak area ratios.

Interpretation of the data in Table 4-15 leads to the following conclusions:

- the measured ambient concentrations of naphthalene and anthracene are a strong function of sample site location and correlate positively with the percent downwind parameters, suggesting that they are indeed compounds emitted by the Kosovo coal gasification plant.
- there is a clear distinction in chemical speciation and pollutant concentration between the vapor samples on the Tenax and the particulate samples on the HiVol filters: Tenax samples are found to contain species from benzene to pyrene at the $\mu g/m^3$ level, HiVol samples contain PNAs mostly heavier than anthracene but at levels in the ng/m^3 range ($\sim$1000 x lower).

It should be pointed out that the relative concentrations of benzene and toluene are minimum values due to the demonstrated vapor breakthrough of these species in the sample collection on Tenax.

TABLE 4-15. COMPARATIVE CHEMICAL PROFILE OF KOSOVO AEROSOL AND VAPOR PHASE SAMPLES COLLECTED ON DAY 5 AT SITES #1, #3 AND #4

COMPOUND NAME	MW	SITE 1(0.6% DW)		SITE 3(18.7% DW)		SITE 4(40.0%DW)	
		TENAX	HIVOL	TENAX	HIVOL	TENAX	HIVOL
benzene	78	303	ND	20	ND	89	ND
toluene	92	565	ND	76	ND	101	ND
C_2 - alkyl benzene	106	442	ND	107	ND	131	ND
C_3 - alkyl benzene	120	260	ND	123	ND	141	ND
C_4 - alkyl benzene	134	40	ND	30	ND	40	ND
naphthalene	128	100%*	ND	100%*	7%	100%*	ND
methyl naphthalene	142	35	ND	26	ND	50	6
acenaphthene	154	15	5	11	ND	17	ND
fluorene	166	43	2	7	ND	8	5
anthracene phenanthrene	178	33	100%*	15	100%*	19	100%*
fluoranthene	202	ND	1.4	3.5	76	1.9	230
pyrene	202	ND	1.6	3.1	97	1.6	240
chrysene benzanthracene triphenylene	228	ND	ND	ND	ND	ND	360
benz( )pyrenes benz( )fluoranthenes perylene	252	ND	ND	ND	ND	ND	1100
Ambient air concentrations of naphthalene or anthracene, μg/m³ AIR (= 100% normalized value)		0.2*	-	1*	0.001*	3*	0.003*

*Relative concentrations in upper table are normalized to naphthalene for vapor and anthracene for particulate; lower table presents absolute ambient concentrations calculated for these two species only.

TABLE 4-16. COMPARATIVE CHEMICAL PROFILE OF KOSOVO AEROSOL AND VAPOR PHASE SAMPLES COLLECTED AT SITE #4 ON DAYS 5, 6, 7, AND 8

COMPOUND NAME	MW	DAY 5(40.0%DW)		DAY 6(45.2%DW)		DAY 7(39.4%)		DAY 8(18.4%DW)	
		TENAX	HIVOL	TENAX	HIVOL	TENAX	HIVOL	TENAX	
benzene	78	89	ND	31%	SOXHLRT MALFUNCTION	11	ND	20	
toluene	92	101	ND	41		43	ND	44	
C_2 - alkyl benzene	106	131	ND	73		72	ND	76	
C_3 - alkyl benzene	120	141	ND	56		60	ND	76	
C_4 - alkyl benzene	134	40	ND	26		25	ND	38	
naphthalene	128	100%*	ND	100%*		100%*	23%	100%*	
methyl naphthalene	142	50	6	43		35	ND	24	
biphenyl	154								
acenaphthene	154	17	ND	9.0		10	ND	8.3	
fluorene	166	8	5	9.3		7.3	9	4.7	
anthracene	178	19	100%*	20		14	100%*	11.2	
phenanthrene									
fluoranthene	202	1.9	230	2.7		3.6	230	2.5	
pyrene	202	1.6	240	2.2		2.3	230	1.6	
chrysene									
benzanthracene	228	ND	360	ND		ND	370	ND	
triphenylene									
benz( )pyrenes									
benz( )fluoranthenes	252	ND	1100	ND		ND	940	ND	
perylene									
Ambient air concentrations of naphthalene or anthracene, $\mu g/m^3$ AIR (= 100% normalized value)		3	0.003	5		2	0.003	2	

*Relative concentrations in upper table are normalized to naphthalene for vapor and anthracene for particulate; lower table presents absolute ambient concentrations calculated for these two species only.

Examination of the data in Table 4-16 indicates that the concentrations of selected pollutants in the air samples showed only small variations on a day to day basis at the downwind Site #4 during the sampling period day 5-8 (May 18-21, 1979).

A GC-MS mass chromatogram of the downwind Tenax resin sample #1022 is shown in Figure 4-24, with selected ion traces for mass 78, 128 and 202 characteristic of benzene, naphthalene, and fluoranthene/pyrene, respectively. A similar mass chromatogram for the downwind HiVol filter extract #132 is shown in Figure 4-25, with selected ion traces at masses 202, 228 and 252, characteristic of PNA isomer groups.

The aromatic profile of the vapor phase of the ambient air samples was qualitatively the same whether the Tenax resin aliquot was separated by solvent extraction or by thermal desorption, as can be seen in Table 4-17.

Correlation of Organic Loading with Percent Downwind--

Disregarding the possibility of real day to day variations in pollutant concentrations, all measured concentrations of naphthalene can be plotted against the measured percent downwind value for the particular day and site. The data in Tables 4-15 and 4-16 is plotted in Figure 4-26 to determine the degree of correlation between organic vapor loading and percent downwind. A linear regression analysis gave the following results for this plot:

Slope = 0.0826 $\mu g/m^3$/percent downwind
Intercept = 0.034 $\mu g/m^3$
Coefficient Correlation = 0.85

Thus, the ambient air concentration of naphthalene as collected on the Tenax cartridges correlates positively with the percent of time that the sampling site was downwind of the Kosovo gasification plant. The extrapolated concentration of naphthalene at 100% downwind is 8.2 $\mu g/m^3$.

Comparison of Chemical Species in the Ambient Air Sample and Medium Oil--

More than 50 compounds and isomers were tentatively identified by GC-MS in the Kosovo vapor phase samples. It was of interest to determine the correlation between the chemical speciation of the ambient air samples and that of the coal gasification facility's by-products. A positive correlation would support the conclusion that the sampling program was successful in collecting samples characteristic of the gasification plant's emissions.

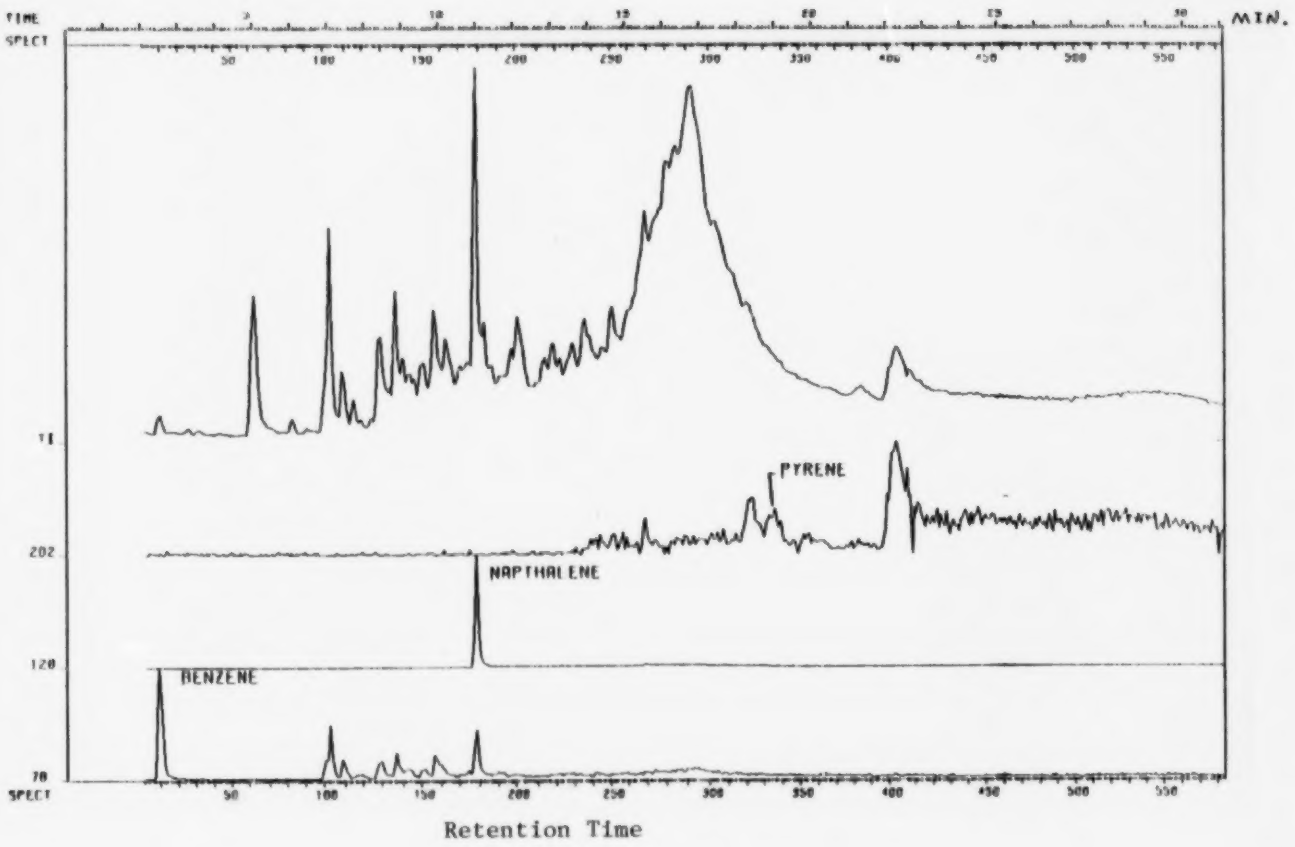


Figure 2-24. GC-MS Chromatogram of Downwind Tenax Sample #1022, Total Ion Current and Selected Ions at Mass 78, 128, and 202 AMU

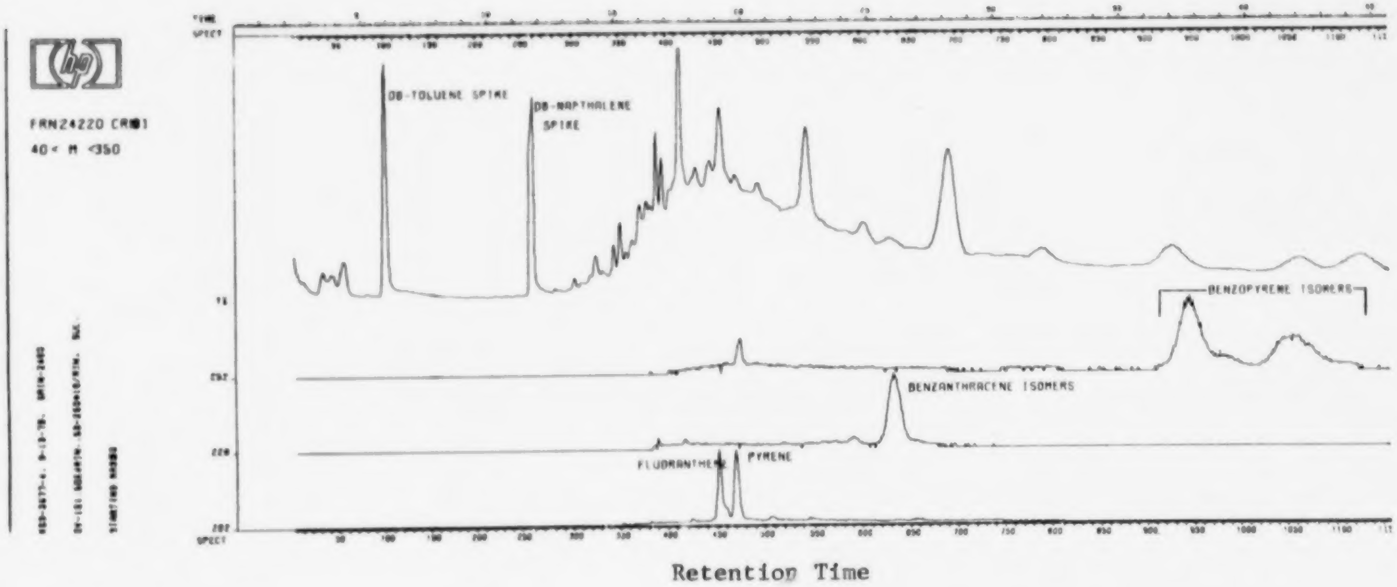


Figure 4-25. GC-MS Chromatogram of Downwind HiVol Filte 32, Total Ion Current and Selected Ions at Mass 202, 228, and 252 AMU

TABLE 4-17 COMPARISON OF THERMAL DESORPTION AND SOLVENT EXTRACTION ON TENAX RESIN #1022 (DAY 6, SITE #4, FRONT)

COMPOUND NAME	MW	THERMAL DESORPTION	SOLVENT EXTRACTION
benzene	78	31%	ND
toluene	92	41	30%
C_2 - alkyl benzene	106	73	58
C_3 - alkyl benzene	120	56	33
C_4 - alkyl benzene	134	26	10
naphthalene	128	100%*	100%*
methyl naphthalene	142	43	29
biphenyl			
acenaphthene	154	9.0	5.9
fluorene	166	9.3	6.2
anthracene	178	20	9.8
phenanthrene			
fluoranthene	202	2.7	2.5
pyrene	202	2.2	2.1
chrysene			
benzanthracene	228	ND	ND
triphenylene			
benz( )pyrenes			
benz( )fluoranthenes	252	ND	ND
perylene			

*Relative Peak quantitation is normalized to naphthalene.

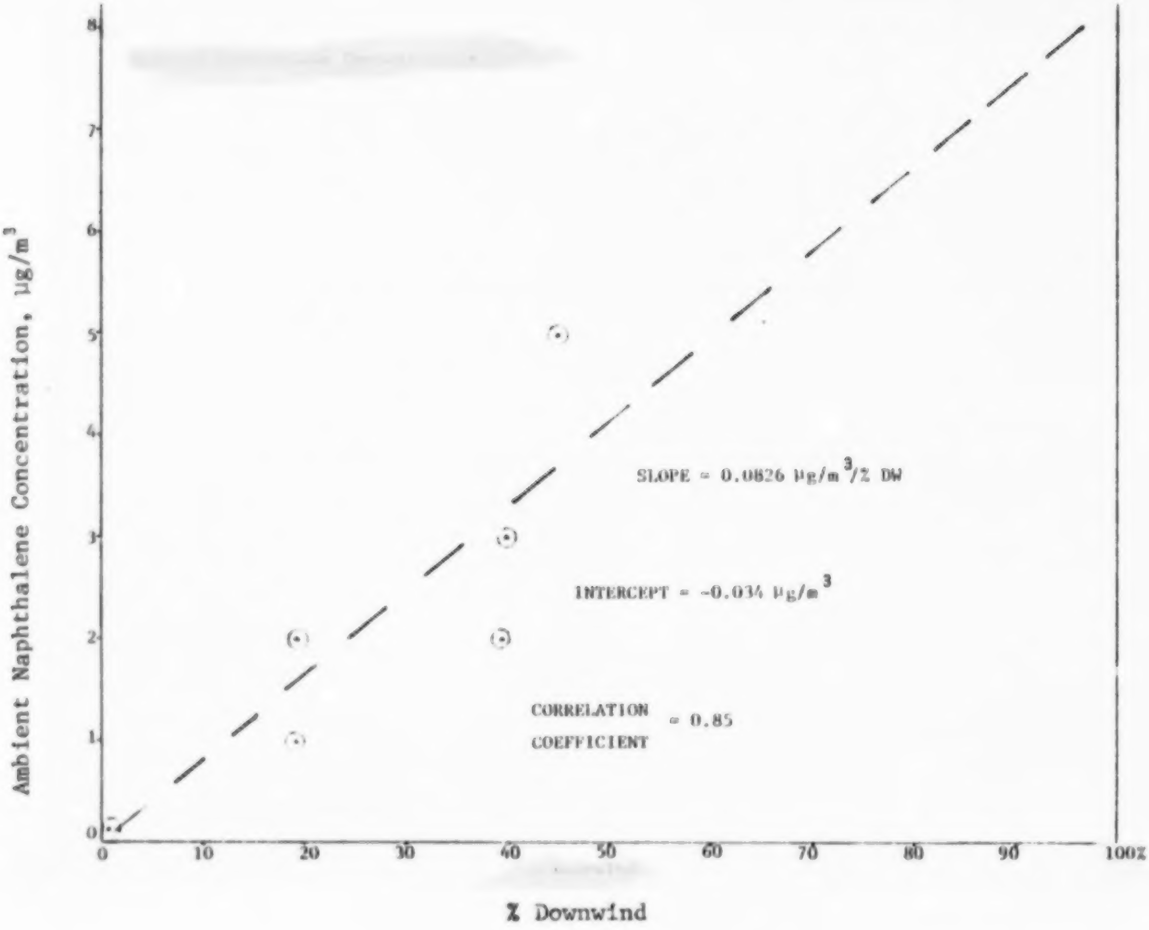


Figure 4-26. Correlation of Organic Loading in Kosovo Ambient Air with the Percent of Time the Sampling Site was Downwind of the Coal Gasification Plant

The following gasification plant by-products were analyzed concurrently with the air samples:

- medium oil, in solution and spiked onto Tenax,
- medium oil, basic compounds extract,
- tar, in solution, and
- heavy tar, in solution.

In Tables 4-18 the chemical species profiles are compared for the day 5 downwind Tenax resin sample (#1029) and HiVol filter (#132) and the medium oil.

It can be seen that essentially all of the species identified in the ambient air samples can also be detected in the medium oil. Therefore, the species identified in the samples collected from the surrounding atmosphere can be considered characteristic of the air emissions from the Kosovo Lurgi coal gasification plant.

Comparison of the Compounds in the Ambient Air Samples to Ambient Air Goals--

In Table 4-19, several of the measured compound concentrations in the ambient air are compared with the corresponding MEG Ambient Level Goals (A-MEG) based on certain health effects. The ambient air compound concentrations are derived from the measured values, extrapolated to 100% downwind.

The A-MEG concentration goals are probably exceeded in the Kosovo aerosol for benzene, phenol and benzo(a)pyrene.

TABLE 4-18. COMPARISON OF CHEMICAL SPECIES PROFILES IN KOSOVO AMBIENT AIR SAMPLES AND MIDDLE OIL

COMPOUND OR ISOMER GROUP IDENTIFICATION	MOL. WT.	NO. ISOMERS DETECTED	NORMALIZED CONCENTRATIONS		
			TENAX	HI VOL	MEDIUM OIL
	HYDROCARBONS				
benzene	78	1	89	ND[2]	24%
toluene	92	1	101	ND	23
C_2-alkyl benzenes	106	≥3	131	ND	20
C_3-alkyl benzenes	120	≥6	141	ND	17
C_4-alkyl benzenes	134	≥9	40	ND	15
naphthalene	128	1	100%[1]	ND	100%
methyl naphthalenes	142	≥2	50	6%	34
acenaphthene	154	1	17	ND	8
fluorene	166	1	8	5	10
anthracene/phenanthrene	178	≥1	19	100%[1]	18
methylanthracene	192	≥2			8
fluoranthene	202	1	1.9	230	3.2
pyrene	202	1	1.6	240	3.0
chrysene benzanthracene triphenylene	228	≥1	ND	360	1.2
benz(a and e)pyrenes benz(b and k)fluoranthene perylene	252	≥3	ND	1100	0.5
terphenyl	230	≥3	ND	300	0.4
trimethylphenyl indane	236	1	1.4	ND	0.2

[1] Absolute concentration of naphthalene = 3 $\mu g/m^3$, anthracene = 0.003 $\mu g/m^3$.

[2] ND = Not detected by GC-MS.

TABLE 4-18. (Continued)

COMPOUND OR ISOMER GROUP IDENTIFICATION	MOL. WT.	NO. ISOMERS DETECTED	NORMALIZED CONCENTRATIONS		
			TENAX	HI VOL	MEDIUM OIL
	C-H-O COMPOUNDS				
phenol	94	1	87	ND	18
methyl phenols	108	≥2	83	ND	44
C_2-alkyl phenols	122	≥5	67	ND	43
acetophenone	120	1	6	ND	3
dibenzofuran	168	1	13	ND	9
diphenylquinone	260	1	33	ND	ND
phthalate ester @ 14.4 min.		1	7.7	300	4.0
phthalate ester @ 17.5 min.		1	11.3	3000	5.6
	C-H-S COMPOUNDS				
methyl thiophene	98	2	4	ND	1.9
C_2- alkyl thiophenes	112	≥4	8	ND	2.8
C_3- alkyl thiophenes	126	≥3	ND[3]	ND	1.8

[3] ND = detected by HECD-N analysis; not detected ($\lesssim$1%) by GC-MS due to hydrocarbon interference.

TABLE 4-18. (Continued)

COMPOUND OR ISOMER GROUP IDENTIFICATION	MOL. WT.	NO. ISOMERS DETECTED	NORMALIZED CONCENTRATIONS		
			TENAX	HI VOL	MEDIUM OIL
	C-H-N COMPOUNDS				
pyridine	79	1	D[3]	ND	100%[4]
methyl pyridines	93	≥2	D	ND	790[4]
C_2- alkyl pyridines	107	≥4	D	ND	830[4]
C_3- alkyl pyridines	121	≥5	D	ND	640[4]
quinoline	129	1	D	ND	600[4]
isoquinoline	129	1	D	ND	100[4]
methyl quinolines	143	≥5	D	ND	320[4]
C_2- alkyl quinolines	157	≥10	D	ND	150[4]

[4] Detected and quantified in the basic extract of middle oil, normalized to pyridine.

TABLE 4-19. COMPARISON OF COMPOUNDS IN THE AMBIENT AIR TO AMBIENT AIR GOALS

CHEMICAL SPECIES	AMBIENT LEVELS AT 100% DW $\mu g/m^3$	A-MEG GOALS $\mu g/m^3$
1. benzene	6.8[1]	7.1
2. naphthalene	7.5	100
3. benzo(a)pyrene	0.08[2]	.00005
4. phenol	6.0	3.8
5. methyl thiophene	0.3	41
6. pyridine	0.08	36

[1] Minimum benzene concentrations because of breakthrough.

[2] Quantitation of all mass 252 isomers.